



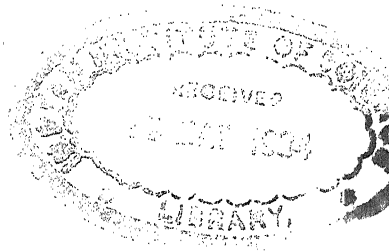
# CRITICAL STUDIES IN THE LEGAL CHEMISTRY OF FOODS

FOR CHEMISTS, FOOD INSPECTION OFFICIALS AND  
MANUFACTURERS AND DEALERS IN FOOD PRODUCTS

BY

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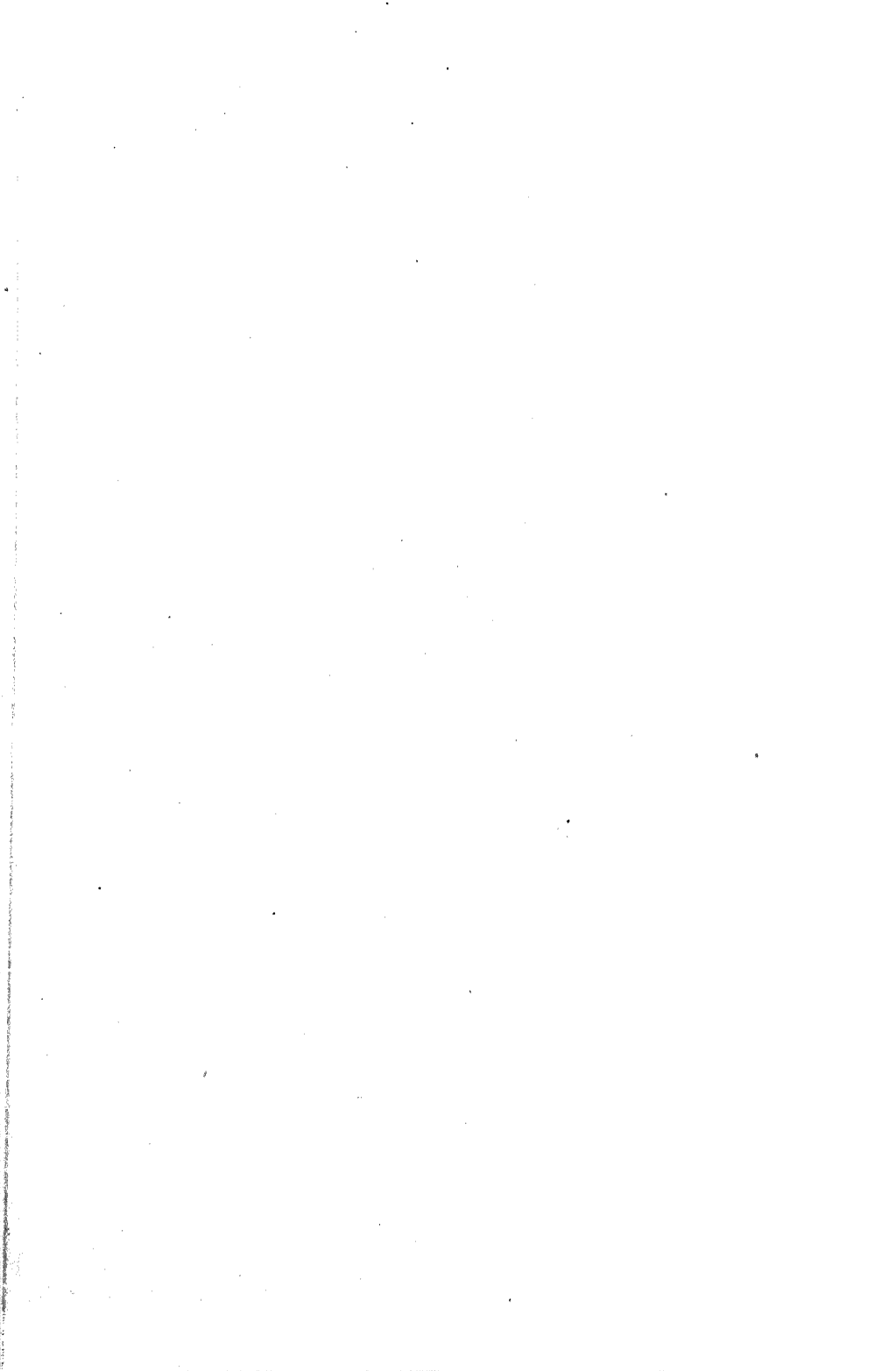


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## DEDICATION

Dedicated to my former colleagues in pioneer food control work, Messrs. Wiley, Bigelow, Frear, Browne, Doolittle, Leach, Winton, Ladd, Alsberg, Seeker, Street, Hortvet, Lythgoe, Tolman, Ogden and Bryan, to whom I gratefully acknowledge the use of many valuable data determined by them as a "labor of love" during their busy official careers.



## PREFACE

Much of the matter included in this volume has been compiled and written by the author in his capacity as Consulting Scientific Editor for various technical and trade journals, and has hitherto been scattered in various issues of these journals over a period of some fifteen years. Many requests for back numbers containing this or that article, together with the advice or suggestions of scientific acquaintances and clients, have prompted him to assemble, revise and publish the articles in one compact reference manual.

The author has always attempted to give the latest, fairly complete science of the subject under consideration in language sufficiently simple to be understood by any intelligent layman, as well as by chemists and food law attorneys; and to indicate or interpret for the guidance of chemists, attorneys, manufacturers and dealers the significance of the chemical facts and compiled data with reference to food inspection laws, regulations and, particularly, food standards.

Practically all data on the composition of various food products were determined by the "Official & Tentative Methods of Analysis of the A. O. A. C.", specified in Regulation No. 4 of the "Rules & Regulations for the Enforcement of the Food & Drugs Act" (Circular No. 21 of the Office of the Secretary of the United States Department of Agriculture); and on commercial and laboratory-made products of known purity, the data in the various chemical journals and Federal, State and Canadian food inspection reports were used. Thus, from various official Canadian reports the data on practically all the well-known brands of English jams and marmalades were obtained, and from the many and exhaustive reports of the United States Bureau of Chemistry and the Connecticut State Experiment Station, many valuable data, little known to the average chemist and layman, were obtained.

The author has been connected with food inspection work for nearly thirty years, as an official chemist in active state inspection work and as an analytical and consulting expert for the food industry, and has prepared the evidence and furnished expert testimony in more than four hundred court cases and hearings involving some

ninety different food and drug products. The need of accurate, modern data on samples of known purity in connection with the interpretation of food inspection laws, regulations and standards was very early forced upon him; likewise the need of explaining intricate chemical and biological facts in the simplest language possible.

An occasional repetition of a statement or standard will be noticed in the text, in Chapter III, mainly. This is necessary as certain readers will be interested only in that portion of the text dealing with their own particular manufactured product.

R. O. BROOKS.

New York City,  
August 1, 1927.

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# CRITICAL STUDIES IN THE LEGAL CHEMISTRY OF FOODS

## Chapter I.

### The Legal Chemistry of Fruits and Fruit Products.\*

Just why, in the economy of nature, various trees, bushes and vines should surround the seeds resulting from their reproductive efforts with a cellular pulpy mass of water, fiber, sugars, pectin compounds, fruit acids, tannin and mineral salts, is not fully known. The most probable explanation is that by drying and slow decomposition afterwards, the pulpy mass protects the seed from sinking into the ground and germinating until climatic and other conditions are favorable, as in the spring.

By cultivation, breeding and cross-breeding man has so increased the size, quality and number of these seed-carriers that they constitute one of our most important sources of food and also one of the most acceptable from a gastronomic standpoint. They were, of course, the first vegetable foods of prehistoric man, the cultivation of cereals and tubers developing later.

In shape, nearly all fruits are a modification of the sphere, indicating an outward growth of pulp cells in all directions, the external cellular matter having the power of forming a more or less hardened coating or skin. In the case of certain fruits the seeds are more or less completely embedded in the exterior surface, but in the majority of cases the seeds are in an inner hardened case or series of cases, as in the peach and apple, for instances.

In view of the fact that practically every fresh fruit is largely composed of water (ranging from 60 to 90 percent), it is evident that a cellular structure is indispensable to preserve form and more or less rigidity. These cells are usually minute and multitudinous in all fruits and the cell-walls are composed largely of insoluble cellulose, lignin

\* Originally published in *The Fruit Products Journal and American Vinegar Industry*, Oct., 1923. *et seq.*



and related substances known as pecto-celluloses. When the cell-wall substances ferment (as in fermented pomace for example) slimy, gummy substances (pentosans, galactans, etc.) are formed from the original constituents and it becomes possible to rupture a larger proportion of fruit cells and obtain a larger proportion of a juice on pressing. This juice, however, is abnormal in composition and not as acceptable for various purposes as the juice from fresh, unfermented fruit.

Rotting is the result of a series of putrefactive fermentations, whereby the cell-wall material is completely decomposed and the contents of the cells likewise, resulting in a soft, usually dark-colored, ill-tasting spot. The fermentations causing rot may be due to microorganisms (molds, bacteria and yeasts) gaining entrance through some abrasion or insect puncture, or in some cases rotting is apparently caused by ferments (enzymes) naturally present in the fruit itself.

Cold storage causes a temperature unfavorable for the growth of microorganisms or the rapid action of naturally present enzymes. The changes taking place in a fruit during ripening are largely due to action of enzymes, which convert the earlier formed starch, etc., into sugars (sucrose, or ordinary sugar, dextrose and levulose, known as reducing sugars), gums (pectins) and esters which give the flavor characteristic of a given fruit.

Experiments have shown that a definite respiration is progressing meanwhile, which continues while the fruit is in storage. Those interested in the details of this respiration should consult Bulletin 94 of the Bureau of Chemistry of the U. S. Department of Agriculture. Here a large amount of data are reported on the ripening and "breathing" of apples and a quite complete résumé is given of other investigations on the changes taking place during the ripening and storage of various fruits.

These changes, like any other series of chemical action, involve variations in temperature and thus we have an explanation of the heating and spoilage of fruits in unventilated storage and transit and the "sweating" of fruits in other cases. In general it can be shown that most fruits are in a continual state of change until cooking has destroyed all life activities and sterilization has prevented action due to microorganisms in the dead tissues and juices.

The "ripening point" may be considered as that point where the sugar content reaches the maximum. In the apple this occurs just about the time the last traces of starch disappear, although the relative proportions of the various sugars present continue to change dur-

ing storage, to the enhancement of the fruit juice, cider and vinegar-making value of the apples.

Considerable investigation of the various changes occurring during the ripening of citrus fruits (oranges and grapefruit particularly) has been carried on under the direction of Dr. R. E. Rose, State Chemist of Florida. This was begun because of the custom of picking green oranges, causing them to turn yellow by a "sweating" process, and then selling them, although far from ripe. On account of the nature and distant source of the banana, this selling of an unnaturally yellow, half-ripe fruit may be necessary, but with the orange and grapefruit it is not necessary.

The results of the investigation showed that the lowest ratio of sugars (as invert sugar) to fruit acid (citric acid) consistent with an acceptable degree of maturity, was seven to one, i.e., that an orange or grapefruit should contain at least seven times as much total sugar (as invert sugar) as it contained of acid (as citric acid). In addition it was recommended that state standards be fixed that would prevent the shipment of all oranges showing more than 1.3 percent of total acid (as crystallized citric acid) and 1.75 percent for grapefruit. In the case of oranges, color was not found to be of deciding value in judging the ripeness of the fruit. Green-colored fruit was sometimes found to be ripe for picking and shipment, yellow fruit was frequently found to be unripe.

The cell-wall material of fruits, as said above, is largely composed of insoluble cellulose and related substances, and after all juice has been pressed out and any remaining soluble matters leached out it constitutes the "marc" or "insoluble solids" of the fruit or fruit product.

In the case of the apple this marc, constituting about 2 percent of the whole apple, is about one-half pure cellulose. The analytical item known as "crude fiber" is mainly cellulose. The cell-wall material, small as is the proportion in the whole fruit, is so built up into myriad cells as to hold nearly all the remaining substances in the fruit as a watery solution, or in some cases (olive for instance) as an oil-water emulsion.

The chief constituents of interest and commercial value which are dissolved in the water of a ripe fruit are the three sugars mentioned above as derived largely from fruit starch during ripening, the fruit acids (which vary in different fruits) and the pectin or jelly-forming substance. Much work has recently been done on the commercial utilization of pectin substances; several trade forms of "pectin" are

being sold to the public and preserving trade for jelly making, etc., with considerable success, in cases of making a jelly from fruit juices deficient in pectin, or obtaining a stiff jelly with a minimum of any fruit juice. The chemistry of pectin is still obscure, but some very good investigations have been carried out recently on the degree of fruit acid concentration (in terms of hydrogen-ion concentration), and the percentage of sugar and pectin necessary to get best results in legitimate jelly making. A number of these are referred to elsewhere.

As to the legality of added pectin, the U. S. Bureau of Chemistry announces in Service and Regulatory Announcement, Chemistry 27, Item 370, that "in the preparation of jellies and similar products from fruits deficient in pectin, no objection is made to the addition of pectin in small quantities when such addition does not serve to conceal damage or inferiority, provided the presence of added pectin is declared on the label, and provided further that the pectin has been prepared from clean and sound material. The employment of substantial amounts of fruit or fruit juices is assumed."

Inasmuch as the use of commercial pectin has given rise to a class of deceptively labeled products containing little or no fruit juice, it is further announced that "A food product sold under the name 'jelly' unqualified, or qualified by a fruit name, or not distinctly qualified to show that it is not a fruit product, should contain fruit juice in substantial quantities. Products made from sugar and commercial pectin with natural or artificial fruit flavors and colored to simulate fruit jellies are regarded by the bureau as imitation jellies, which the law requires to be labeled with the word 'imitation' together with a statement plainly indicating them to be imitations, such as a declaration of the ingredients."

The fruit acids found in different fruits are as follows: *l*-malic acid in the apple (from 0.1 percent in "Sweet Bough" to 1.11 percent in "Red Astrachan"), and in cherries, gooseberries, apricots, quinces and peaches; citric acid in oranges, lemons (about 7 percent), grapefruit, strawberries (one-tenth of acid is malic), raspberries, pineapples (one-eighth of acid is malic), currants, blackberries, cranberries (also contain benzoic acid), huckleberries, gooseberries, pears and tomatoes; tartaric acid and salts of same in grapes; and succinic acid in certain unripe fruits. All of these acids are white crystalline soluble substances, intensely sour, and the sweetness of a fruit depends entirely upon how much of the fruit acid is dissolved in the juices in the cells and not on the percentage of sugar present. Many intensely sour fruits contain more sugar than those containing less fruit acid and therefore

tasting sweeter. The Concord grape contains both malic (60 percent) and tartaric (40 percent) acids.

Tannin or "tannic acid" is an interesting constituent of fruits, being the cause of the puckering effect on the mouth membranes produced by crab-apples, quinces, persimmons, etc. In the manufacture of high grade apple ciders, as in France and Germany, much attention is paid to the tannin content, as high as 1 percent being tolerated and at least 0.3 percent demanded in the apples used. The bittersweet taste of French cider apples is due to tannin and proportions of sugars running as high as 26 percent in some varieties.

The rapid browning of fruit flesh (apple, for instance) after the contents of the cells have been exposed to the air by crushing or cutting is due to the oxidation of tannin by the enzyme oxidase (present in the fruit) in the presence of oxygen of the air. In evaporated fruits this is prevented by exposing to fumes of burning sulfur, which incidentally, acting as a preservative also, allows considerably more water to be sold than would be possible in old style dried fruits. Tannin, in brown bruised places in ripening fruits, will prevent the conversion of starch into sugars, also.

The fatty oil, found in small proportion in certain fruits, is usually a constituent of the seeds and this is also true of the nitrogenous substances (vaguely reported as "protein"). In the olive, the fatty oil is in an emulsion form in the flesh surrounding the seed.

The flavor of fruits is due to minute proportions of complex mixtures of esters, aldehydes and aromatic or terpene alcohols, ketones and hydrocarbons. Power and Chestnut have analyzed the flavoring oil of the apple (mainly in the skin) and reconstructed an apple flavoring oil of very satisfactory quality, composed of iso-amyl formate, acetate, caproate and caprylate; geranyl formate and acetate; geraniol and acetaldehyde. They have also analyzed the flavoring substances of peaches, while oil of orange, lemon and the flavoring substances of grapes (methyl anthranilate especially) are fairly well known chemically.

The mineral salts present in fruits have not been separated as such to any great extent, although very complete analyses of the mineral residue ("ash") left on burning fruits and fruit juices have been made, showing nearly always alkaline carbonates, phosphates, and other simple salts resulting from the decomposition of more complex mineral salts, etc., in the fruit itself, during burning. In the "ash" of the apple, for instance, about 68 percent of potassium carbonate and 22 percent of potassium and magnesium phosphates is found. The alkalinity of

the "ash" and other data on it are of considerable value in judging the purity of various fruit products.

### FRESH AND DRIED FRUITS

In the Federal Food Standards (Food Inspection Decision 203, Office of Secretary, U. S. Dept. of Agriculture), fruits are defined as the "clean, sound, edible, fleshy fructifications of plants, characterized by their sweet, acid and/or ethereal flavors . . . Fresh fruit is fruit which has undergone no material change other than ripening since the time of gathering. . . . Dried fruit is the clean, sound product resulting from the evaporation of the greater part of the water from properly prepared fresh fruit. . . . The term 'sundried' is commonly used to designate the product dried without the use of artificial heat. The terms 'evaporated' and 'dehydrated' are commonly used to designate the product dried by the use of artificial heat."

Only a few of the fruits are legally standardized as yet, although quite a number of fruit products are. There are three Federal Food Inspection Decisions to date dealing with citrus fruits (Nos. 133, 150 and 182), in which standards or certain prohibitions are given. Food Inspection Decision 133 deals with the artificial coloring (by "sweating" or other methods) of immature oranges and it is pointed out that such oranges do not change in sugar or fruit acid content after picking, but would ripen properly if left on the tree. Further there is stated to be evidence that such immature oranges are apt to cause serious disturbances of the digestive system, especially in children, and it is the opinion of the officials in charge of food inspection work that such oranges are "colored in a manner whereby inferiority is concealed and are, therefore, adulterated."

Food Inspection Decision 182 definitely fixed certain standards for oranges and grapefruits, as follows:—"Oranges (common, sweet or round) are the sound, mature fruit of *Citrus sinensis*, Osbeck. The juice of the mature fruit contains not less than eight (8) parts of soluble solids to each part of acid, calculated as citric acid without water of crystallization. Grapefruit, pomelo, is the sound, mature fruit of *Citrus grandis*, Osbeck. The juice of the mature fruit contains not less than seven (7) parts of soluble solids to each part of acid calculated as citric acid without water of crystallization." \*

Food Inspection Decision 150 dealt with frozen citrus fruits. Such

\* See page 51 for more data, especially on ripeness indices of cantaloupes, water-melons and honeydew melons.

fruit is injured in flavor by freezing or frost and soon becomes dry and unfit for food, a bitter taste developing and a decrease in sugar and fruit acid resulting. The Decision holds that such fruit is "inferior and decomposed within the meaning of the Food and Drug Act." Such fruit will be regarded as adulterated "if the contents of any package found in interstate commerce contains 15 percent or more of citrus fruit which, on a transverse section through the center, shows a marked drying in 20 percent or more of the exposed pulp."

These official regulations give us a little idea of how such simple natural food products as whole fruits are liable to official standardization for various purposes. In Service and Regulatory Announcement No. 21 of the Bureau of Chemistry we have other regulations. Thus the term "Crab Apple" must not be applied to ordinary apple products (apple juice or cider); fruits that are sold as "peeled" (peeled peaches) must have the skin *completely removed*.

It is held immaterial whether the peeling is done by cutting or by the use of lye or other chemicals, provided that the product "is not changed in composition or properties by the operation, as might result, for example, by insufficient washing after lye peeling." Another regulation requires that the label state if grated pineapple contain any cores or trimmings, the latter being indicated by the presence of portions of the "eyes" and horny skin leading inward to the "eye."

The geographically incorrect labeling of fruit comes under food law control. Thus California figs, even though grown from Smyrna stock, must not be sold as Smyrna figs. A number of regulations deal with weights of solid fruit when packed with water or syrups in cans.

Definite standards for certain dried fruits are in force or in preparation. The legal standard for "Evaporated Apples" specifies same to be "made from peeled, cored and sliced apples, and to contain not more than twenty-four (24) percent of moisture, as determined by the official method of the Association of Official Agricultural Chemists." "Canned fruit" is defined as the "clean, sound product made from properly prepared fresh fruit, with or without water and/or sugar (sucrose), (a) by processing in a suitable hermetically sealed container, or (b) by heating and packing in a suitable container which is then hermetically sealed."

"Cold-pack" fruit is defined as "the clean, sound product obtained by packing, in a suitable container, properly prepared fresh fruit, with or without the addition of sugar (sucrose), and maintaining it at a temperature sufficiently low to insure its preservation."

The analyses shown in Table 1, although not pretending to repre-

Table 1. Composition of Various Fruits.

Fruit	Total Solids	Insoluble Solids	Ash	Acidity (as $H_2SO_4$ ) Percent	Ordinary Sugar	Reducing Sugar	Crude Fiber
Apples							
Minimum	9.35	1.80	0.17	0.07	0.15	5.34	0.70
Maximum	23.36	2.75	0.40	0.86	7.75	11.75	1.98
Apricots							
Minimum	12.75	4.82	0.45	0.56	0.80	4.69	....
Maximum	18.75	7.76	0.82	1.09	6.25	9.92	5.27
Bananas							
Minimum	21.60	2.23	0.70	0.17	4.99	3.16	....
Maximum	34.55	4.52	1.10	0.43	16.20	17.70	....
Blackberries							
Minimum	12.06	4.72	0.45	0.55	None	4.44	....
Maximum	16.42	9.06	0.82	0.86	0.50	4.74	5.21
Cherries							
Minimum	12.64	2.04	0.38	0.33	None	6.84	0.62
Maximum	22.30	6.25	0.73	1.63	0.30	13.32	6.07
Currents							
Minimum	12.97	....	0.60	1.57	None	3.44	3.22
Maximum	15.23	6.90	0.72	1.62	None	6.38	5.57
Figs					Total Sugars		
Minimum	11.46	....	0.36	0.07	8.00		
Maximum	38.84	....	1.16	0.29	20.99		
Grapes							
Minimum	12.82	....	0.38	0.25	1.23	6.56	...
Maximum	22.29	....	0.59	0.40	10.67	14.92	....
Grapefruit							
Minimum	9.94	1.17	0.39	0.54	3.11	1.69	....
Maximum	13.29	2.70	0.46	0.59	4.77	3.12	....
Guava							
Minimum	19.61	11.75	0.63	0.37	0.16	2.84	....
Maximum	22.14	15.21	0.84	0.64	0.91	6.07	....
Lemons							
Minimum	14.37	2.43	0.61	4.42	0.99	1.28	....
Maximum	15.23	2.98	0.98	5.50	1.22	2.98	....
Limes							
Minimum	14.77	3.82	0.67	4.80	None	0.34	....
Maximum	14.84	3.97	0.98	5.52	0.16	0.42	....
Mamey Colorado							
Minimum	29.24	....	0.80	0.07	0.29	5.20	....
Maximum	34.01	6.55	0.89	0.10	16.85	20.78	....
Mamey Santo Domingo							
Minimum	14.12	4.49	0.31	0.39	5.49	2.50	....
Maximum	15.74	....	0.38	0.42	5.64	3.92	....
Mango							
Minimum	10.23	0.82	0.35	0.09	7.19	1.72	....
Maximum	21.72	3.70	0.78	0.39	11.99	6.14	....
Oranges							
Minimum	11.38	0.56	0.35	0.16	None	3.15	....
Maximum	14.81	2.70	0.57	2.02	6.75	10.33	....
Peaches							
Minimum	14.24	....	0.44	0.42	0.87	2.10	....
Maximum	16.60	....	0.79	0.48	6.30	5.60	....
Pears							
Minimum	16.77	2.98	0.31	0.02	4.36	8.26	2.77
Maximum	20.12	4.85	0.45	0.21	....	9.00	4.30
Persimmons (Japan)							
Minimum	18.52	3.45	0.39	Tannin		14.52	....
Maximum	25.06	5.29	0.49	0.13		17.75	....
Pineapples							
Minimum	10.78	1.02	0.27	Acidity		1.76	....
Maximum	18.86	1.83	0.55	0.30		9.75	....
Plums							
Minimum	15.14	5.05	0.52	0.60	3.56	2.50	4.34
Maximum	21.60	8.12	0.61	1.25	....	9.40	....
Raspberries							
Minimum	13.16	6.62	0.49	0.37	None	3.52	....
Maximum	18.79	8.59	0.77	1.11	0.83	6.59	5.90
Sapota							
Minimum	21.01	8.39	0.38	0.07	0.08	7.34	....
Maximum	25.47	9.90	0.56	0.20	2.54	14.50	....
Strawberries							
Minimum	6.85	2.57	0.37	0.67	0.02	2.72	1.03
Maximum	12.38	3.01	0.81	1.18	1.16	6.71	2.26

\* Includes the pits.

sent all compiled data on different varieties of fruits, will give a general idea of how different fruits analyze, how the water, sugar and fruit acid content vary. For convenience in making comparisons the acidity is arbitrarily calculated in terms of sulfuric acid, although, of course no fruit actually contains any free sulfuric acid.\*

As illustrating the changes taking place upon drying fruits, the data on evaporated apples shown in Table 2 are of interest.

Table 2. Analyses of Evaporated Apples.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	9.35	28.88
Total solids .....	71.12	90.65
Sucrose .....	15.31	22.72
Reducing sugars .....	29.92	42.84
Acidity (as malic acid) .....	3.75	4.10
Total ash .....	1.07	1.74
Insoluble solids .....	7.54	15.24

The sample showing but 9.35 percent moisture was a dark colored, home-dried product, and it shows, as compared with the other data, how the commercial sulfuring process allows much more water to be sold as dried apple flesh on account of the preservative qualities of the sulfurous acid coming from the burning sulfur used to prevent darkening of the apple slices.

Food Inspection Decision 76, which regulates the use of preservatives and dyes in foods, states that no prosecution will be instituted "in the case of the application of fumes of burning sulfur (sulfur dioxide), as usually employed in the manufacture of those foods and food products which contain acetaldehyde, sugars, etc., with which sulfurous acid may combine, if the total amount of sulfur dioxide in the finished product does not exceed 350 milligrams per kilogram (in solid products), of which not over 70 milligrams is in a free state."

The sulfuring process is in practically universal use for drying sliced apples and is also used more or less with apricots, prunes, raisins and other fruits. The result is that we have "dried fruits" being sold which are not fully dry, fruits containing as close to the legalized limits for moisture as can be guessed at by the operators of drying plants, and fruits which on standing continue to lose appreciable proportions of moisture, according to the condition of the air, especially its dryness. It also stands to reason that fruits containing close to the legal maximum of moisture will, under suitable humid conditions, begin to take up more moisture, soon becom-

\* See page 12 for acids actually present.



ing an illegal product, (excess of 24 percent apple moisture) and, unless the sulfur dioxide remaining therein be dangerously near to or in excess of the proportions allowed in Food Inspection Decision No. 76, will begin to get moldy and show evidences of decay. Quite a few shipments of decayed dried fruit have been seized and condemned to destruction during the operation of food law inspection, especially Federal inspection.

Also when trying to put out "dried fruits" as close to the legal moisture maximum as possible, it happens frequently that the maximum is exceeded and a food inspection prosecution is then warranted, even for the slightest excess of moisture the food inspection chemist is sure of. The legal maximum (or minimum) tolerance in a food standard is a scientifically-legally generous limit to accommodate an exceptional, probably abnormal case, but much too often has it been seized upon by the trade as a "selling standard," witness the cases of milk fat in milk, milk solids in evaporated milks, acidity in vinegar and moisture in dried apples. If the trade persists in this unforseen practice, they will have to install much more exact and scientifically checked-up (by chemical analysis) methods of manufacture, or else risk prosecution, as the maxima and minima in food standards were never intended as "selling standards," and if the official chemist is sure of his figures, then a prosecution is warranted for the slightest digression. This does not seem to be realized by many in the trade circles. The "selling standard" should be nearer to the normal average, not some generous legal minimum or maximum tolerance.

As to further losses in the moisture content of dried fruits on standing, the Connecticut State Experiment Station at New Haven published considerable data in its 1912 report which are of interest to give here and of interest also in connection with statements of net weights on packages of dried fruits, as required under the Federal Food Laws. Packing close to a net weight declaration, of a product which is liable to lose moisture on account of insufficient drying, is running a legal risk, or at least the embarrassment of having to prove the net weight at time of packing.

In the Connecticut State Experiment Station study of moisture losses in dried fruits, one hundred and two samples were examined. For a full discussion of the results one should consult Bulletin 172 of that station. It was undertaken primarily to study the variations in the weight of dried fruits sold in package form and the losses in weight of those packages after keeping for several months.

In the twelve samples of dried or "evaporated" apples examined, two-thirds of them were labeled "sulfured," although in most of them the sulfur had disappeared during storage. Fifty percent of the samples showed some decay, due probably to excess of moisture in the absence of sufficient sulfur-compound to exert a preservative action. Packages marked as containing one pound when packed showed from 14 to 15 ounces when purchased and after seventy to eighty-five days storage these figures had dropped to about 13 ounces. Thus we have losses of three or more ounces out of an original 16 ounces or approximately 19 percent! Some samples of originally 16 ounces had lost 6 ounces in similar storage periods, or approximately 38 percent!

Probably most of these were short weight to start with, but one can readily see the risks involved in insufficient drying, in trying to sell too close to a legal maximum tolerance of 24 percent moisture. During an average storage period of about 75 days in the Experiment Station, the average loss on all samples examined was about 2 ounces or about 12.5 percent. In no brand was this supplementary storage loss less than half an ounce and in this case it is evident that much loss of moisture had already taken place preceding purchase, as the net weight was only 11 ounces.

In apricots, sulfur bleaching had also been practiced and the final weights, after an average supplementary storage period of 70 days, ranged from 12.7 ounces to 13.6 ounces, showing average losses of 2 ounces during said storage. One of the apricot samples was in bad condition, showing decay, live worms and insect casts.

All but two of the eighteen samples of dried currants were labeled as being cleaned or washed. Currants are not bleached with sulfur and therefore a more thorough drying is necessary, as the preservative properties of the sulfur cannot be figured upon. The average storage period (after purchase) was about 75 days and the average loss only about one ounce. One sample in fact was sufficiently dry originally to have taken up moisture (over 2 ounces increase). This shows that the storage atmosphere at the Station was not especially dry, and that the "dried fruits" kept there were not subjected to any unusual storage conditions. The two samples not marked as "cleaned" showed high percentages of "acid-insoluble ash," which would be a measure of adhering dirt or sand. Properly cleaned dried currants should not show much over 0.25 percent acid-insoluble ash.

Eight samples of dates were kept in storage between 133 and 144 days. Here is another fruit not dried with sulfur fumes and evi-

dently sufficiently dry when packed to have lost little moisture. The average loss in the average 140 days' Station storage period was about one ounce, or about 6 percent on a 16 ounce basis at time of purchase.

Figs are practically always "prepared" or rendered soft and moist with a glucose or sugar solution, hence they are not really a "dried fruit" after such treatment, but rather a moistened fruit. The losses on storage would be fairly large in a dry atmosphere, but in an ordinary moist atmosphere there would be an absorption of moisture due to the very sugary nature of the fruit. This refers to layer figs as prepared for dessert or confection purposes. The whole dried figs, imported in large quantities largely for grinding up into "fig paste," are usually quite dry and absorb rather than lose water.

The Connecticut State Experiment data did not include dried peaches and pears. Some data from other sources show fresh commercial dried peaches to average about 22 percent moisture and pears of similar grade to average 23 percent moisture. Peaches and pears would act practically the same as apricots and apples (see above) in storage losses due to selling in so moist a condition.

Prunes, excepting "Ruby prunes," are not sulfured, but there is a tendency to sell them moist so as to grade them as large as feasible. Samples kept for 133 to 150 days in storage at the Connecticut State Experiment Station showed further losses of about 2 ounces which if originally 16 ounces gave a final moisture loss of 3 to 5 ounces. An average of 4 ounces moisture loss would be a 25 percent loss of weight.

Only one of thirty-two samples of raisins contained sulfur-compounds, this being a brand of Sultana raisins. Raisins are perforce well dried, therefore the moisture losses were small. The supplementary storage period averaged about 80 days and the average loss about half an ounce, or about 3 percent.

The housewife has plenty of water at her disposal and, if her wishes were consulted, would probably prefer buying fruit flesh rather than an excess of fruit water. The author can see no valid reason for a loss of more than 10 per cent on the original weight at the most, and in most products this loss could be kept lower with advantage to all most concerned.

According to the method of estimating moisture used, there are unavoidable errors of 1.5 to 4 percent in the work of skilled analysts and when a fruit dryer tries to sell within one or two percent of a maximum legal tolerance he is courting trouble. The most approved method is drying in an efficient vacuum oven at 70° C. for twelve hours. Apples, however, will give practically the same result in

four hours in an ordinary oven at the temperature of boiling water. For the analysis of raisins and certain fruits particularly rich in sugars, the meat-chopper ground fruit should be mixed with about half its weight of finely divided asbestos, moistened and mixed well with distilled water, evaporated barely to dryness over a water-bath and then dried in the vacuum oven as in the analysis of the other fruits, after they have first been mixed and quickly ground up fine as practicable.

### FRUIT JUICES

Fruit juices are obtained usually by pressure from grated or (in case of grapes and berries) whole fruit. Under the influence of pectin, provided the percent of sugar, water and particularly the correct degree of fruit acidity is maintained, the juice will "set" to form a firm jelly. The chemistry of the fruit jellies will be taken up later on. Here we will confine ourselves to the fruit juices, as beverages and as the basis of fruit syrups used in the soda fountain trade.

Fresh fruit juices are frequently sold as such and legal standards are being fixed for certain ones. They are also sold in concentrated form (syrup) and in carbonated form as "sparkling" fruit juices. Mixed with sugar they are used in large quantities as "fruit syrups," for the soda fountain trade.

The fermented fruit juices constitute the wine industry, using the term wine in a broad sense. Thus fermented grape juices constitute the ordinary wines; fermented apple juices are called ciders or apple wines, constituting in certain parts of Europe an industry rivaling the grape wine industry; fermented pear juice is known as "perry"; in addition we have blackberry and currant wines, raisin wines from dried raisin grapes and more recently wines from the fermentation of orange and peach juices.

In this discussion we shall not endeavor to take up these fermented products. It would serve only painfully to remind us of a happy past and how legislative bodies sometimes tear down a whole edifice in order to get rid of one or two objectionable occupants. From a scientific and medical standpoint there is a vast difference between a fermented beverage and a distilled alcoholic drink. One is a strictly natural product with a very low alcohol content, the other is an artificial product with a dangerously high alcohol content. Just now the dangerous drinks (imitation and true whiskies, gins, brandies and rum) are available and the harmless, innocent fermented beverages

not available. Thus runneth the usual course of fanatical "reformers," as distinguished from sane experts.

The commonest fruit juice is, of course, apple juice, but grape juice is a close second and lime juice, orange juice and other fruit juices are increasing in importance as articles of commerce.

The proposed standard for "fresh fruit juices" defines them as the "clean, unfermented liquid product obtained by the first pressing of fresh ripe fruit." The standard for apple juice ("apple must") defines it as the "fresh fruit juice obtained from apples, the fruit of *Pyrus malus*," and fixes the following analytical limits: "specific gravity (20° C.) not less than 1.0415, nor greater than 1.069; contains in one hundred (100) cubic centimeters (20° C.) not less than six (6) grams and not more than twenty (20) grams of total sugars in terms of reducing sugars, not less than twenty-four (24) centigrams nor more than sixty (60) centigrams of apple ash, which contains not less than fifty (50) percent of potassium carbonate."

The requirement in the proposed standard that the fruit shall be ripe is especially desirable in the case of the apple in order to avoid a slimy, turbid juice due to suspended apple starch, which, if the fruit were ripe, would have been converted into sugars. Ripe apples and ripe fruits generally, excepting the banana, contain no starch. Other suspended gummy substances, etc., will cause fruit juices to be distinctly turbid. In the case of orange juice this turbidity is desired, but with apple juice it is now customary to filter so as to sell only a bright clear product, especially if sold in glass containers.

Pasteurization, in glass containers, is apt to flatten the flavor of a fruit juice more or less. The choice of a more acid variety of the fruit in question will offset this to some degree.

The amount of juice and particularly the proportion of valuable sugars obtainable from the apple (and some other fruits as well) by means of the average press is seldom much over 50 percent of the amount contained in the apple. In eight varieties of thoroughly pressed summer apples the average proportion of the total sugars of the apples left therein was 47.1 percent and for eleven autumn varieties, 44.7 percent. In other words, nearly half of the total sugars in the apple are lost unless "second pressings" are utilized.

Table 3 is not necessarily a complete compilation, but will show the general range in composition of different fruit juices. The acidity is expressed in terms of sulfuric acid, for convenience in comparing relative acidity, as the actual fruit acids themselves vary in nature, according to the kind of fruit (see preceding paragraphs).

Table 3. Composition of Fruit Juices.

Fruit		Total Solids	Ash	Acidity (as H <sub>2</sub> SO <sub>4</sub> )	Ordinary Sugar	Reducing Sugars	Sugar-free Solids
Percent							
Apples*							
Minimum	.....	10.16	0.24	0.07	0.30	4.67	3.37
Maximum	.....	18.81	0.41	0.91	7.05	11.63	4.36
Apricots							
Minimum	.....	10.75	0.40	0.70	0.95	4.75	3.89
Maximum	.....	16.25	0.62	1.05	6.50	10.45	4.41
Blackberries							
Minimum	.....	7.14	0.35	0.57	none	4.25	3.63
Maximum	.....	8.94	0.47	1.48	0.40	8.60	4.56
Cherries							
Minimum	.....	11.80	0.38	0.21	none	9.50	3.95
Maximum	.....	19.65	0.62	1.46	0.20	13.40	9.40
Currants							
Minimum	.....	6.71	0.30	1.07	none	4.61	2.66
Maximum	.....	15.70	0.76	2.03	none	9.96	7.50
Grapes							
Minimum	.....	11.51	0.22	0.23	1.23	6.67	1.41
Maximum	.....	30.67	0.70	0.42	10.67	24.92	6.13
Grapefruit							
Minimum	.....	8.03	0.37	0.59	3.20	1.75	
Maximum	.....	11.50	0.44	0.65	4.90	4.02	
Huckleberries							
Minimum	.....	10.02	0.23	0.35	0.06	6.42	3.05
Maximum	.....	11.40	0.32	0.78	0.34	7.70	3.70
Lemons							
Minimum	.....	8.05	0.28	4.61	none	1.66	
Maximum	.....	12.66	0.44	5.68	1.32	3.50	
Limes							
Minimum	.....	7.80	0.26	4.72	none	0.12	
Maximum	.....	9.10	0.38	5.80	0.16	0.40	
Loganberries							
Minimum	.....	8.70	0.24	0.80	none	4.34	2.80
Maximum	.....	11.82	0.62	1.50	0.35	8.04	4.00
Oranges							
Minimum	.....	10.38	0.30	0.25	none	2.90	
Maximum	.....	14.21	0.52	2.20	5.30	8.20	
Peaches							
Minimum	.....	12.00	0.30	0.42	3.50	2.01	3.57
Maximum	.....	14.60	0.58	0.60	7.15	6.19	3.78
Pineapples							
Minimum	.....	8.70	0.24	0.25	1.45	4.84	
Maximum	.....	14.00	0.44	0.48	6.61	11.00	
Quinces							
Minimum	.....	10.41	0.30	0.28	none	7.24	
Maximum	.....	12.14	0.48	0.61	none	8.90	
Raspberries							
Minimum	.....	6.92	0.34	0.78	none	3.64	3.45
Maximum	.....	12.63	0.74	1.12	0.80	8.60	5.59
Strawberries							
Minimum	.....	6.01	0.32	0.58	none	2.59	2.20
Maximum	.....	12.14	0.60	0.92	0.40	8.54	3.98

\* Not including French cider apples, which sometimes test as high as 26 percent total sugars.

By "second pressings" should be understood a product obtained by macerating the pomace (residue from first pressing) immediately with a small definite proportion of water and repressing. Such a product is usually almost as rich in sugars as a first pressing (Browne\* reports 8.4 percent of sugars in an ordinary "second pressing"), and even though possibly not acceptable as a fruit juice the regulated use of same (especially when standardized) should be allowed in the manufacture of a legal apple vinegar, and the Federal standard for the so-called "cider" vinegar modified to provide for the same. The preferable strength vinegar for table purposes contains from 4 to 4.5 percent acetic acid, and a second pressing, such as the above-mentioned one, would furnish an apple vinegar of this strength upon proper fermentation.

At one time these "second pressings" were largely utilized by boiling down to form a "cider" jelly ("boiled cider"), which, mixed with spirit vinegar or dilute acetic acid, was quite successfully used to adulterate or imitate genuine apple vinegar. The "cider jelly" can also be used for reinforcing compound and imitation jams and jellies. Browne reports 51.7 percent sugars in a sample of "cider jelly" made from "second pressings," 44.5 percent being water.

The successful marketing of a fresh fruit juice, such as apple, grape or lime juice, is an uncertain proposition. Of the three, grape juice appears to be most capable of being put on the market in sterile condition, without resorting to the use of preservatives. The use of sulfites for preserving bottled lime juice was once universal, while for apple juice it is generally claimed that an acceptable, well flavored product can not be marketed except by use of a preservative. The legally tolerated sodium benzoate is now generally used, but many manufacturers claim salicylic acid to be superior as an apple juice preservative.

There are being put on the market, however, bottled apple juices, preserved only by sterilization or pasteurization with heat and hermetical sealing, similar to bottled grape juice, and Gore at the Bureau of Chemistry in Washington reported on a number of experiments in preserving apple juice in barrels, tins and glass by heat and hermetical sealing alone (Bulletin 118, Bureau of Chemistry). For complete details the reader should send for this bulletin (no charge), and read carefully. Briefly, it was found possible to quickly remove the bulk of the suspended insoluble matter in fresh apple juice by the ordinary milk separating machine. The juice was then pasteur-

\* Pa. State College Report 1901-2.

ized, by passing through a tin coil heated by a jacket of steam, at a temperature of 65° to 70° C. (149° to 158° F.). It was then passed directly into well-made casks which had been paraffined internally and rendered sterile internally by the following process:

After paraffining, live steam was run into the cask for three minutes, then a small amount of sulfur was burned in a suspended small cup inside the cask, after which it was allowed to stand closed over night and just before filling with juice was steamed out again for three minutes and rinsed with hot (sterile) water to remove the sulfurous products. After filling with hot juice, a bung which had been paraffined and kept in alcohol, and which contained a quarter-inch hole through the center stuffed with cotton was immediately inserted, and when the juice had cooled to normal temperature a paraffined wooden skewer, sterilized in alcohol, was forced into the hole in the bung, displacing the cotton. This, when cut off and the end coated with a drop of paraffin, constituted a permanent air-tight seal.

Casks filled thus kept indefinitely, and if opened and the contents removed carefully did not ferment within a reasonable length of time. In sealed tin cans and glass containers, the juice was sufficiently pasteurized to prevent spoilage by heating in a stirred water-bath at about 155° F. for three-quarters of an hour, allowing an extra half hour in the case of glass, for the contents of the bottle to attain the temperature of the bath. All of the above prepared products had a slight cooked taste, and probably a real expert on the flavor of apple juices would have detected a loss of the delicate apple flavoring esters, etc., at least in the barrel products.

For the manufacture and preservation of grape juice the reader should send for and carefully read Bulletin 24 of the Bureau of Plant Industry, U. S. Department of Agriculture. A somewhat higher temperature is necessary and can be safely used in pasteurizing the juice of the grape. It should not be heated, however, above 195° F., and from 165° to 175° will usually give a sterile product. The details as outlined here would probably serve for preserving the grape juice in casks.

The proposed Federal standard for grape juice defines and standardizes it as "the fresh fruit juice obtained from grapes (*Vitis* species), has a specific gravity (at 20° C.) not less than 1.040 and not exceeding 1.124; and contains in one hundred (100) cubic centimeters (20° C.) not less than seven (7) grams nor more than twenty-eight (28) grams of total sugars in terms of reducing sugars, not less than



Table 3a. Analyses of Grape Juices.

Variety (No. of samples)	Specific Gravity	Total Solids	Total Sugar (as reducing)	Non- Sugar Solids	Acidity (as tartaric)	Free Acid (tartaric)	Acid Potassium Tartarate	Total Ash	Alkalinity of Soluble Ash (N/10 acid)	Polarization (normal weight)	Alcohol (per cent by volume)
Concord (417)											
Minimum .....	1.055	14.08	10.41	1.70	0.40	0.01	0.36	0.22	19.0 cc.	-4.3°V.	0.02
Maximum .....	1.089	23.43	20.48	3.61	1.82	0.42	0.84	0.41	47.2	-7.0°V.	0.37
Average .....	1.074	18.48	16.25	2.75	0.99	0.21	0.54	0.30	28.9	-6.0°V.	0.12
Catawba (242)											
Minimum .....	1.051	16.47	12.77	1.73	0.51	0.01	0.37	0.23	19.7	-5.0°V.	0.01
Maximum .....	1.093	25.17	22.85	3.79	2.03	0.41	0.73	0.40	42.4	-7.5°V.	0.44
Average .....	1.080	22.50	19.40	2.61	1.09	0.24	0.56	0.34	30.7	-6.3°V.	0.20
Clinton (58)											
Minimum .....	1.054	17.05	14.01	2.49	0.86	0.00	0.87	0.48	46.4	-5.8°V.	0.00
Maximum .....	1.103	27.78	23.48	4.79	2.56	0.37	1.25	0.70	69.6	-7.9°V.	0.55
Average .....	1.095	22.70	19.49	3.62	1.62	0.19	1.07	0.60	57.5	-6.7°V.	0.17
Delaware (109)											
Minimum .....	1.073	18.56	16.65	1.78	0.44	0.00	0.38	0.25	20.4	-6.1°V.	0.03
Maximum .....	1.108	29.23	26.85	4.25	1.53	0.38	0.84	0.49	46.2	-8.3°V.	0.46
Average .....	1.097	24.98	22.59	2.43	0.76	0.17	0.57	0.37	32.1	-7.2°V.	0.18
Ives (101)											
Minimum .....	1.055	14.56	10.76	1.50	0.38	0.00	0.50	0.29	26.4	-4.4°V.	0.00
Maximum .....	1.080	22.72	21.22	4.74	1.15	0.26	0.84	0.44	44.4	-7.2°V.	0.39
Average .....	1.069	18.15	15.06	2.78	0.71	0.11	0.67	0.36	35.1	-5.9°V.	0.19
Norton (72)											
Minimum .....	1.049	18.66	14.81	2.92	0.75	0.00	0.87	0.53	50.8	-5.9°V.	0.01
Maximum .....	1.100	30.55	27.00	6.13	2.21	0.27	1.40	0.65	74.0	-8.9°V.	0.45
Average .....	1.092	25.68	22.09	3.82	1.31	0.13	1.15	0.59	61.9	-7.1°V.	0.14

twenty (20) centigrams and not more than fifty-five (55) centigrams of grape ash and not less than fifteen (15) milligrams nor more than seventy (70) milligrams of phosphoric acid ( $P_2O_5$ )."

Hartman and Tolman have determined the amount of volatile acid (as acetic acid), nitrogen, sulfur and phosphoric acid ( $P_2O_5$ ) on various Concord grape juices and find the following proportions:

	Grams per 100 cc.	
	<i>Minimum</i>	<i>Maximum</i>
Volatile acid (as acetic) .....	0.01	0.04
Nitrogen .....	0.043	0.054
Sulfur (as $SO_2$ ) .....	0.007	0.012
Phosphoric acid ( $P_2O_5$ ) .....	0.015	0.041

They also determined the volatile esters (as ethyl acetate) in nineteen samples of Concord grape juice, finding from 0.12 to 0.23 gram, with an average of 0.16 gram per 100 cubic centimeters of juice.

The most characteristic ester giving flavor to grape juice is methyl anthranilate, which has a decided grape odor and which is being extensively used to reinforce juices and to prepare imitation grape beverages. It actually exists in various true grape juices, but in very small proportion, being most plentiful in red juices of the Concord type, where 0.0002 gram per 100 cubic centimeters of juice has been reported.

For various other fruit juices, these methods of preservation sometimes work; at other times there is such a loss of flavor and color as to interfere with the sale of the product. In Bulletin 241 of the U. S. Department of Agriculture is reported a long series of experiments on a large number of fruit juices, which develop the fact that ordinary methods (as above) could be successfully applied to the juices of black raspberries, blackberries, currants, sour cherries and peaches. Other methods utilizing refrigeration and sterilization in carbon dioxide were tried with other fruit juices. The following is a summary of the results generally.

*Pressing.*—Satisfactory yields of juice were easily obtained from all of the fruits studied. Lemon and orange juices were best expressed by cutting each fruit into several pieces and then pressing, a method which could be successfully used in pressing pineapples, although the method of pressing the fruit without previous cutting is probably superior. It was found advisable to pass all of the other kinds of fruit pressed, without heating, through an apple grater to facilitate the outflow of the juice.

Heating before pressing in the case of black raspberry, blackberry,

red currant, black currant and huckleberry juices resulted in larger yields of juice and the development of more color and a more distinctive flavor than were obtained from cold pressing. Strawberries, red raspberries, cherries, peaches, pineapples, lemons and oranges were cold pressed.

Heating the juices sufficiently to sterilize them did not injuriously affect the color of any of the fruit juices, though pineapple, lemon and orange juices usually darkened somewhat if heated in the presence of dissolved oxygen or if exposed to atmospheric oxygen during the heat treatment.

The distinctive flavor of the fresh fruit was greatly injured and the familiar cooked strawberry taste appeared when strawberry juice was sterilized by heat. The fresh fruit flavor of orange juice\* was also distinctly injured when the juice was heated. Although all lost in the quality of freshness, heating did not seriously affect the flavor of other fruit juices, except in cases where the heat employed was excessive.

*Retention of Distinctive Colors and Flavors.*—The extent to which color and flavor were retained on keeping the juice after sterilization varied greatly in the juices from the various fruits.

In strawberry juice the brilliant red color of the freshly sterilized juices in all cases faded greatly and further flavor losses occurred. Sterilization and subsequent keeping in carbon dioxide were not effective in securing color retention.

Red currant juice very gradually lost in distinctive color and flavor on being kept at room temperatures after sterilization, and keeping in carbon dioxide was not effective in securing either color or flavor retention. Cold storage at from 32° to 35° F. was found to be a very satisfactory means of controlling color and flavor changes.

The distinctive colors and flavors of black currant, blackberry and black raspberry juices were satisfactorily retained during prolonged periods at common storage. The flavor of blackberries was, however, distinctly less well retained than that of black currants or black raspberries, though it did not undergo a perceptible change during a storage period of six months.

In the case of red raspberries the distinctive color and flavor were

\* Hall and Wilson, of the Research Laboratory of the California Fruit Growers' Exchange, have recently investigated the volatile flavoring constituents of Valencia orange juice and find present: alcohol, acetone, acetaldehyde, formic acid, an olefin alcohol ( $C_{10}H_{18}O$ ), isoamyl alcohol, phenylethyl alcohol and esters of formic, acetic and caprylic acids.

poorly retained, even on keeping the juice in carbon dioxide in cold storage at from 32° to 35° F.

When sterilized and subsequently kept in carbon dioxide the distinctive color of pineapple juice remained practically unchanged. When exposed to atmospheric oxygen at juice surfaces during and after sterilization, marked darkening occurred. Change in color was also found to be greatly, though not wholly, retarded by keeping the juice in cold storage at from 32° to 35° F. On keeping the juice at ordinary temperatures the distinctive pineapple flavor gradually lessened, though the juices remained recognizable as pineapple. By keeping in cold storage at from 32° to 35° F. flavor change was almost wholly prevented.

The distinctive colors and flavors of peach and cherry juices were quite well retained while kept at room temperatures. Huckleberry juice, hot pressed, lost in flavor on keeping.

Lemon juice darkened in color if sterilized and kept in the presence of atmospheric oxygen, though the color was satisfactorily retained when the juice was sterilized and kept in carbon dioxide or in vacuum. In all cases an off-flavor, designated as a "bottled lime-juice" flavor, appeared in the lemon juice after it had been kept for a time after sterilization, even though in cold storage at from 32° to 35° F.

Orange juice also underwent a marked darkening in color when kept at room temperatures after being sterilized. The color was fairly well retained when atmospheric oxygen was excluded by sterilizing the juice and subsequently keeping it in vacuum or in carbon dioxide, and the change in color was well controlled by keeping the juice at low temperatures. The flavor of sterilized orange juice, already slightly injured by the heating necessary for sterilization, underwent further changes when kept at room temperatures. It was found that by keeping the juice in cold storage at from 32° to 35° F. the flavor was well retained for long periods.

*Keeping in Freezing Storage, and Concentration by Freezing.*—The distinctive colors and flavors of all fruit juices kept in freezing storage at about -10° C. (14° F.) were found to remain practically unchanged during many months, except that a peculiar coagulation of much of the coloring matter appeared in the juice of the black raspberry. It was possible to concentrate fruit juices to syrups by freezing out the water as ice and centrifuging. Characteristic colors and flavors were well retained on concentrating.

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*Filtering.*—Infusorial earth greatly promotes the filtering of fruit juices, as it retards greatly the clogging of the filter.

*Conclusion.*—Juices of red and black currants, blackberries, black raspberries, sour cherries and peaches may be prepared easily and successfully on a large scale by the methods used for the preparation of grape juice, as they retain their characteristic properties well on being sterilized and stored. Strawberry juice and red raspberry juice are not suited for preparation on a large scale because of the readiness with which the distinctive colors and flavors change. Huckleberry juice is somewhat characterless. Pineapple juice requires special methods for its successful preparation which are not necessary in case of the other juices. Its preparation on the commercial scale, however, is of marked promise.

Satisfactory methods for the preparation of lemon and orange juices have not been developed. The peculiar change in flavor of lemon juice stored after sterilization, even at low temperatures, is an obstacle to be overcome before the preparation of the juice on a large scale can be considered advisable. The problem of preparing orange juice is not without promise. It is not unlikely that highly specialized methods in which cold storage will play a prominent, if not dominating, part will be required."

Relative to artificially carbonated fruit juices the term "sparkling" was for a time forbidden by the food inspection authorities as misleading, inasmuch as it had been used to describe ciders and wines in which the carbonic acid gas (carbon dioxide) existed as a product of the fermentation, as in champagne. On account of prohibition legislation, these naturally carbonated beverages are officially extinct in this country and in Service and Regulatory Announcement, Chemistry 26 it is stated that the term "sparkling" on fruit juices which are clearly unfermented is no longer regarded as deceptive or misleading. In the same announcement the term "champagne" is restricted to the naturally carbonated wines and is considered as "false and misleading" and as constituting a "misbranding under the Food and Drugs Act when used in connection with, and to describe such products as artificially carbonated grape juice or apple juice."

Grape juice and apple juice prepared thus have been long on the market and no doubt others have been prepared at various times. Moreover, carbon dioxide gas has been suggested and tried out merely as a preservative, as referred to in the summary of the U. S. Bureau

of Chemistry "Studies on Fruit Juices" (Bulletin 241, U. S. Dept. of Agriculture).

The principal way, however, in which fruit beverages reach the consumer admixed with carbon dioxide is via the soda fountain. "Soda" is, perhaps, our national beverage and means simply some carbonated water mixed with a fruit-juice flavored sugar syrup. Frequently it also means carbonated water mixed with a sugar syrup which has been simply flavored with more or less artificial fruit flavors. This latter is an illegal proposition unless indicated to the consumer in some way, as the natural presumption is that "strawberry soda," for instance, contains strawberry juice in sufficient proportion to give a strawberry flavor.\*

### FRUIT SYRUPS

Soda fountain fruit syrups are, or should be, as stated above, sugar syrups flavored with fruit juices. In addition we have fruit flavored syrups ("concentrates") intended for dilution with plain water to produce an "ade" (e.g., lemonade, orangeade, grapeade, etc.) or "squash," or "smash," or "crush," or "punch." We have several official food inspection requirements concerning these products.

Thus in Service and Regulatory Announcement, Chemistry 23, the opinion is given that "terms such as ade, squash, punch, crush and smash, when used in conjunction with the name of a fruit, can be applied correctly only to beverages, either still or carbonated, which contain the fruit or juice of the fruit named. Such terms should not be applied to products flavored only with essential oils or essences."

In Service and Regulatory Announcement, Chemistry 26 the above "opinion" was repeated; and it was pointed out that products flavored only with essential oils or essences should be plainly labeled as imitations. To quote, "The Food and Drugs Act requires an imitation to be labeled with the word 'imitation' together with a statement showing wherein it is an imitation, which ordinarily requires a declaration of those ingredients, such, for example, as essential oil, citric acid, and artificial color, giving the article its principal characteristics." It was further held that "any turbid or 'cloudy' orange, or other fruit-flavored beverage, which does not contain either an appreciable quantity of the juice or the edible portion of orange or other fruit named, should be labeled plainly as an imitation."

\* See appendix (p. 262), for labeling of Beverages and Beverage Materials under the Food and Drug Act.

Right here it may be of interest also to quote from the above-mentioned Service and Regulatory Announcement, Chemistry 26 the official attitude on dealcoholized and non-alcoholic wines, fruit beverages, cordials and liquors. "In the opinion of the Bureau the composition and character of whisky, gin, rum, brandy and articles of similar nature are such that nonalcoholic products identical with them except in alcohol content can not be prepared. The Bureau therefore will regard as misbranded any product designated by these terms, even when it is modified by the word "imitation."

The terms "dealcoholized wine" and "nonalcoholic wine" should be restricted to wine, the fermented grape product, from which the alcohol has been removed without appreciable loss of character-giving constituents other than alcohol, such as the substances which give flavor and bouquet. In labeling such articles the term indicating the absence of alcohol should be printed in direct connection with the word "wine" and with the same degree of prominence. Where a specific designation is used, such as "dealcoholized claret," "nonalcoholic burgundy," the product must be true to type. The expression "dealcoholized wine" is preferred to "nonalcoholic wine," in that it more definitely describes the product.

Beverages not identical in composition and character with dealcoholized wine are considered misbranded if labeled or sold under any representation carrying a direct or indirect suggestion that they are wine, regardless of whether or not an expression indicating the absence of alcohol is used.

In order to harmonize the action of this Bureau in the enforcement of the Food and Drugs Act with the position taken by the Bureau of Internal Revenue in the enforcement of prohibition legislation, exception will not be taken to the term "nonalcoholic" when used on beverages containing less than one-half of 1 percent of alcohol.

Beverages or beverage concentrates prepared from fruit products or synthetic flavors are not properly described by names indicative of alcoholic products or imitations of those products, such, for example, as "nonalcoholic peach cordial" and "nonalcoholic imitation peach cordial."

Of the types of cordials formerly on the market many were of such character that products identical with them, except for presence of alcohol, can not be prepared. The expression "nonalcoholic cordial," or an equivalent term, may be used only where the product

is identical in all respects except alcohol content with the cordial indicated."

No standards have ever been fixed for fruit-flavored syrups used in soda fountain trade and analyses of these products vary so widely (according to the generosity of the maker) in the proportion of fruit juice used that it is of no value to give data here. Those of the trade particularly interested in the preparation of fruit syrups for bottling, their preservation, utility, cost of production, and use in carbonated beverages should by all means consult Bulletin 359 of the California State Experiment Station, wherein the fruit beverage investigations of W. V. Cruess and J. H. Irish are given in full. The bulletin gives a graphic outline of the processes of preparing carbonated beverages from cherries and berries, red and white grapes, apples, citrus fruits and the pomegranate.\*

A fruit beverage which is becoming increasingly popular is that made from the juice of the Logan blackberry, or, as better known, the loganberry. Bulletin 773 of the U. S. Department of Agriculture deals with the general nature and utility of this berry and juices and syrups prepared therefrom. The soda-fountain syrups are made by adding sugar to undiluted juice, the composition running from one part of juice to one part of sugar to as high as three parts of juice to one part of sugar. The chemical data of Table 4 are of interest.

Table 4. Composition of Loganberry Fruit Syrups.

	<i>Minimum</i>	<i>Maximum</i>
Specific gravity .....	1.1297	1.2625
	Percent	
Total solids .....	30.01	55.75
Non-sugar solids .....	1.69	4.06
Reducing sugars .....	11.85	38.94
Sucrose (sugar) .....	none	30.62
Acidity (as citric acid) .....	1.06	1.49
Total ash .....	0.19	0.32

In distinction to fruit-juice flavored sugar syrups, such as generally used for dilution to form a beverage in the soda-fountain trade, there is another class of fruit syrups which contain no added sugar. These are the true fruit-juice syrups made by simply concentrating the original fruit juice to a syrupy consistency. Upon dilution with water they would yield to all intents and purposes the original fruit juice and if the dilution was with carbonated water we would get a "sparkling" fruit juice.

The chief fault with "soda" as a beverage is its sticky, excessive

\* See appendix (p. 235), for abstract by J. H. Irish.



sweetness. This is purposely brought about to make the consumer more thirsty, so that he soon craves more beverage and, if addicted to the "soda" beverage habit, he goes on trying to quench thirst with something calculated to make him more thirsty.

It would seem that right here is the opening for fresh fruit juices, free from added sugar or sugar syrup and, at the drug store fountain, for true fruit syrups containing no added sugar.

The earlier methods of concentrating apple and other fruit juices consisted of evaporating off much of the natural fruit water by means of heat, similar to the boiling down of maple tree sap to make a maple syrup. The trouble with fruit juices concentrated to syrupy form by heat has been the cooked taste usually imparted to the finished product. Evaporation in a vacuum pan or kettle, as in the preparation of concentrated milks ("condensed milk") would do away with the "cooked taste" considerably, but even then the delicate ethereal flavoring substances are likely to be more or less completely lost, as they are in general very volatile esters, aldehydes, etc.

In 1914, H. C. Gore of the U. S. Bureau of Chemistry, in the Yearbook of the U. S. Department of Agriculture for that year, pointed out the way to the manufacture of true fruit syrups, particularly apple syrup and concentrated apple juice and cider, by freezing out the natural fruit water, with no possible loss of delicate flavors. The syrups thus prepared were delicious products, which upon dilution with water were practically identical with the original fruit juice in palatability.

The reader who is interested in this proposition should send for Yearbook Separate No. 639 entitled "Apple Syrup and Concentrated Cider." Briefly the process consisted of freezing the fruit juice, breaking up the "ice" cake into very small pieces and separating the concentrated juice from the frozen water by the use of a centrifugal sieve, as used in the manufacture of granulated sugar. More recently a very great improvement has been effected by stirring the fruit juice during the freezing, whereby a thick mush of very fine ice crystals results, which is then separated from the concentrated juice by a centrifugal sieve.

Much less work and greater yields of fruit syrup result by this new modification, which has already been put into commercial use. Herein lies the chief hope of getting full-flavored fruit syrups without the addition of excessive sugar which, in addition to less transportation charges and better keeping properties than with fresh

juices, will have the full natural flavor of the fruit juice upon dilution with ordinary or carbonated water.

By this method the equivalent of 250 gallons of apple juice can be shipped in a 50-gallon barrel and the product used directly as a syrup (on bread, cereals, etc.) or, by dilution, as a beverage practically identical with the fresh fruit juice. The bulletin by Gore also describes the most approved methods for obtaining apple syrup by evaporation methods in the home or on a commercial scale, except where a vacuum kettle is available.

### FRUIT JELLIES

If the original fruit juice be mixed with the right proportion of sugar, if the percentage of fruit acid be within a certain definite range, and if there be enough pectin present, a further concentration by evaporation yields a gel or jelly of a desirable consistency or firmness.

Fruit jellies are scientific products, although they have never been considered as such by the people who make them. As one writer has remarked, they should be "so accurate scientifically that manufacturers can bring their raw materials together in the proper proportions and be sure to obtain a good, reliable, commercial product." Various experimenters and writers have, in recent years, determined and reported upon the correct proportions of the four determining factors in fruit jelly making and the amount of scientific and technical literature resulting is so voluminous that it is out of the question to review it here. A fairly comprehensive bibliography can be found in the August, 1923 issue of the *Journal of the Association of Official Agricultural Chemists* (page 68) and would-be progressive manufacturers should consult, or have their technical assistants consult, the various papers listed.

Sucharipa, reporting (on page 67 of the above-mentioned journal) on some experiments upon the basic principles of jelly making, shows that with the right proportion of sugar, water, fruit acid and pectin, jellies may be produced with no heating at all, in fact a low temperature and correct evaporation are "promoting factors." The formation of the gel or jelly is not considered as a chemical reaction, but as a coagulation of pectin in a liquid-sugar-acid medium. Long heating and high temperature will destroy the jelly-forming power in pectin. Pectins form jellies increasing in firmness with the methoxyl strength of the pectin. The methoxyl groups in the pectin are split off to

some degree during the gel formation, forming methanol. The solid constituents of a jelly consist of pectins only.

As indicated above, the four determining factors in scientifically correct jelly making are sugar, water, fruit acid and pectin. Concerning the role of acids in fruit jellies, L. W. Tarr says:—"Maintaining pectin, sugar and water as nearly constant as experimental conditions permit, jelly formation is shown to be directly correlated with the hydrogen-ion concentration of the fruit acids. Total acidity may vary over a wide range but the hydrogen-ion concentration at which jelly formation occurs is practically constant, this being pH 3.46 for the purest pectin employed. Furthermore, the hydrogen ions are the sole precipitating agents, the anions exerting no effect that could be observed. The presence of neutral salts does probably reduce the hydrogen-ion concentration at which the jelly can form. And the character of the jelly is also determined by the hydrogen-ion concentration, other conditions being equal."

Campbell in the *Journal of Industrial and Engineering Chemistry*, June, 1920, page 558, and in other journals, reports upon commercial experiments on the formation of apple jelly and summarizes as follows:—"1.25 percent of pectin produces a fine commercial jelly; 1.0 to 0.75 percent of pectin produces a delicate quality similar to home-made jellies; 0.3 percent acidity (in terms of sulfuric acid) is necessary to produce a good quality jelly and 0.27 percent as a minimum and 0.5 percent as a maximum" (both in terms of sulfuric acid) is the permissible range. An excess of sugar produces a soft jelly, while an insufficient amount results in a tough product."

He reports experiments, starting with an apple juice containing 1.69 percent pectin (using one pint of juice to one-half pound of sugar) and gradually reducing the pectin content (by dilution of juice) to only 0.5 percent. The jellies from juices containing 1 percent or less of pectin (with acidity not less than 0.3 percent) were too soft for commercial purposes. These jellies were all cooked products (222° F.) and, as yet, in the commercial and domestic production of fruit jellies, such cooking is customary to bring about the proper evaporation and jelling.

Another investigation of a practical nature is that by Professor Goldthwaite of the Department of Household Science of the University of Illinois, Urbana, Ill. It is reported in the *Journal of Industrial and Engineering Chemistry* for June, 1909, and although since then much has been done along the line of theoretical conditions, as indicated

above, yet the practical working conditions of jelly making as developed by Professor Goldthwaite still hold good.

The investigation was a thorough and somewhat lengthy affair and for full details one should consult the above-mentioned journal. We will give here some of the findings, however. Professor Goldthwaite worked with actual fruit juices, not merely solutions of sugar, acid and pectin as in the more theoretical experiments, and it was found that, irrespective of the kind of fruit juice used, certain practical working data gave best results. Thus a hot fruit juice ready to jell on cooling should have a boiling point of  $103^{\circ}\text{ C.}$  ( $217.5^{\circ}\text{ F.}$ ) and the specific gravity should be close to 1.28 at that temperature.

These figures held good when very different proportions of added sugar were used and with fruit juices of widely varying constitution, indicating that in addition to having the right proportions of acidity and pectin, the question of proper boiling was an important factor in causing the pectin to be precipitated in a continuous mass throughout the volume allotted to it. Unless this precipitation of pectin is just right, the physical texture of the jelly is too loose and we have the well-known phenomenon of "weeping" or the separation of liquid from the spaces between the particles of coagulated pectin.

Goldthwaite was one of the first to point out that the change in pectin in jelly making was more of a physical character than chemical, that the pectin does not undergo any very consequential chemical alteration. Sucharipa's recent study (referred to above) confirms this view, and also points out that the firmness of a jelly, depending as it does on the "methoxyl strength" of the pectin, is liable to be weakened by over-boiling which splits off methoxyl groups.

Moreover, too much boiling of the added sugar in the presence of fruit acid results in too much inversion of the former into dextrose and levulose and in experiments where "invert sugar" (equal proportions of dextrose and levulose) was used in place of sucrose (ordinary sugar) only a syrup and not a jelly resulted.

Some degree of inversion of sucrose is desirable, however, as it prevents crystallization of sugar, and this degree seems to be obtained when close adherence to the temperature and specific gravity given above is practised. It is also better not to boil the sugar and fruit juice together from start to finish, but rather to add the sugar so that it may be boiled with the juice not to exceed one-half the total time of cooking.

As to the desirable degree of acidity in fruit juices, Goldthwaite found about 0.5 percent calculated in terms of sulfuric acid to give

best results. Sweet juices which would not jell, although rich in pectin, formed excellent jellies when tartaric acid was added to bring the acidity of the fruit juice up to about 0.5 percent. Tartaric acid was found to give more superior jellies than citric acid.

More recently lactic acid under the trade name of "Lactart" has been used with success, the acid taste being less harsh. No loss of acid takes place during jelly making, unless a volatile acid has been used. It apparently serves only to precipitate and coagulate the pectin and invert the sugar to a desirable extent.

The proportion of sugar used is an important factor, Professor Goldthwaite points out. Although rather tough jellies can be produced by the proper boiling of fruit juices, yet added sugar from a practical standpoint is an important accessory factor. To make one glass of apple jelly required as much apple juice as would suffice for six glasses when sugar was used. However, too much sugar yields poor results. When too large proportions of water have been used in extracting a fruit, too much sugar is used and this, together with the lowering of acidity and pectin content, yields poor jellies. In crab-apple, pear, plum, peach, apple and grape, about one volume of sugar to one volume of fruit juice gave good results generally, other factors being right.

The total sugar concentration of a jelly must be above 65 percent if mold formation is to be avoided, otherwise the container and contents must be pasteurized. Within certain limits the higher the percentage of pectin in a fruit juice, the lower the amount of sugar to form a jelly. This is where the legitimate use of commercial pectin in jelly making comes in. Dr. Singh, of the University of California, Berkeley, Calif., has reported on this possible saving of sugar in the *Journal of Industrial and Engineering Chemistry* for August, 1922. He finds a definite relation between the amount of acid in fruit juices and the amount of sugar necessary to form jelly and advises increasing acidity to the maximum compatible with flavor in order to save sugar. The pectin can be present to as high as 2 percent, but when from 2.5 to 3.0 percent was present a crust-like formation appeared on the jelly which was not only stiffer but less sweet than the lower layers.

To summarize, it may be said that the precautions for good jelly making are: sufficient acidity (0.3 to 0.5 percent in terms of sulfuric acid); 1.25 to 2.25 percent pectin; added sugar in proportion of one volume to one volume of juice; a temperature of 218° F. and specific gravity of 1.28 (at same temperature) at time of being ready to jell.

If pectin and acid are high, less sugar (three-fourths volume to one volume of juice) can be used, provided a final percentage of at least 65 percent sugar is present in the finished product. Use of pectin should be indicated on the label. (See appendix for article by Jameson on "Pectin for Commercial Jelly-Makers.")

The Federal standard for fruit jellies (see Food Inspection Decision 203 of Office of Secretary, U. S. Dept. of Agriculture) defines them as "the clean, sound, semisolid gelatinous products made by concentrating to a suitable consistency the strained juice, or the strained water extract from fresh fruit, from 'cold-pack' fruit, from canned fruit, or from a mixture of two or all of these with sugar (sucrose)." "Glucose jelly" is jelly in which a glucose product is used in place of sugar (sucrose).

Regarding the use of added pectin in jellies (and jams) we quoted in full the Service and Regulatory Announcement, Chemistry 27, Item 370, governing the situation. The following is the most recent expression of opinion from the U. S. Bureau of Chemistry, which has the principal say in matters of food and drug inspection, as affecting interstate commerce.

Outlining its attitude, Acting Chief W. G. Campbell of the Bureau states that "No objection is made to the use of pectin in minute quantities in the preparation of jellies from fruits deficient in pectin when the pectin is wholesome, when it does not conceal inferiority, and when a statement of its presence appears on the label.

"In most instances in the use of pectin, however, the amount used is very much in excess of that required to supply the natural deficiency in the fruit. We have observed jellies made from pectin with only sufficient fruit juice to impart a fruit color to the finished article. Under the terms of the Food and Drugs Act such products should be labeled 'Pectin Jelly,' followed by a statement that it is colored with a fruit juice. Where the amount of fruit juice present is sufficient to impart definitely and unmistakably its characteristic odor, taste and flavor to the finished product, there is no objection to the label 'Pectin and Raspberry (or other fruit) Jelly.' The word 'Apple' may precede the word 'Pectin' if the pectin is in fact derived from apple. Pectin jellies flavored with extracts, either natural or artificial, and colored either with fruit juice or artificial color in imitation of fruit jelly, fall squarely within the provisions of the law outlined in Item 370.

"The Department's definitions and standards for jam and preserve require that not less than 45 pounds of fruit be used to each

55 pounds of sugar in preparation. Where less than that amount of fruit is used and where proper consistency is obtained by the addition of pectin and excess sugar, the article is no longer entitled to be designated as a jam or preserve. We have encountered a great many products on the market in the preparation of which not more than 10 or 20 percent of fruit was used. Where such articles were artificially colored, we have regarded them as imitations and subject to the requirements of the law for the labeling of imitations. If artificial color is not used the Bureau has not objected to the sale of such articles as 'Pectin, Sugar and Raspberry (or other fruit) Jam (or Preserve).' If the amount of fruit present plus the amount of sugar that would normally be associated with it when prepared into a jam or preserve exceeds 50 per cent of the finished product, the Bureau has not objected to a rephrasing in the order of precedence in the labeling, as for example 'Raspberry (or other fruit) Jam, Sugar and Pectin.' In all these suggested types of labeling you will understand, of course, all the words should be set forth in equal prominence. Where acid is added in preparation of these articles an appropriate declaration of that fact should also be made."

The addition of fruit acid, to get the required proportion necessary to form a good jelly, is fully often as necessary as the addition of pectin. Citric acid from lemon juice or tartaric acid from grapes is generally used, although recently lactic acid (the acid of sour milk) in the trade form of 'Lactart' is being substituted with excellent results. The taste of the latter is a pure sour taste, blending well with every flavor and it does not promote crystallization. Many of the sweet fruits such as peaches, pears, and several tropical fruits, contain too little fruit acid naturally to form a good jelly. Phosphoric acid was formerly much used.

As concerns sugar, it is desirable that a considerable proportion of the added sucrose be 'inverted' (changed into 'reducing sugars' by boiling in presence of fruit acid), but not all of it. The proper condition is reached when the boiling point is about 218° F. and the specific gravity of the hot mixture is 1.28. All germ life is killed during the boiling of the jelly, and the concentration of sugars to from 50 to 75 percent prevents any fermentation or spoilage other than that caused by surface mold growths. By pouring melted paraffin over the solidified jelly, this surface growth of mold can be largely prevented.

As to the chemical composition of fruit jellies, we have compiled a number of analyses below (Table 5). Much depends upon the

proportion of fruit juice used and the practice of different manufacturers in this respect varies greatly, as we have seen above. The substitution of apple juice for other fruit juices, in other than apple jelly, is considerably practised and is adulteration from every standpoint. The estimation of the characteristic malic acid of the apple, together with other chemical data, will usually show any appreciable substitution of apple juice for other and more expensive fruit juices in the manufacture of fruit jellies.

Table 5. Composition of Fruit Jellies.

Fruit	Total Solids	Ordinary Sugar	Reducing Sugars	Total Sugars	Non-sugar Solids	Acidity (as H <sub>2</sub> SO <sub>4</sub> )	Ash
	Percent						
Apple							
Minimum .....	53.90	4.60	20.78	52.08	2.90	0.24	0.10
Maximum .....	66.06	33.04	51.52	63.05	8.10	0.69	0.56
Blackberry .....	59.63	44.90	12.51	57.41	2.22	0.48	0.33
Crab Apple							
Minimum .....	61.12	1.20	18.00	38.60	4.67	0.03	0.10
Maximum .....	66.00	23.68	56.30	58.61	22.52*	0.20	0.30
Currant							
Minimum .....	56.70	3.96	20.20	43.80	0.52	0.09	0.17
Maximum .....	75.03	23.60	58.79	69.25	21.96*	1.57	0.62
Cranberry .....	54.76	2.10	47.20	49.30	5.46	....	0.16
" .....	40.80	8.70	23.60	32.30	8.50	0.96	0.14†
Grape							
Minimum .....	54.10	3.47	32.29	52.81	0.85	0.31	0.21
Maximum .....	72.22	30.52	64.27	67.74	6.53	0.83	0.45
Guava							
Minimum .....	79.14	43.43	30.66	74.89	4.23	0.47	0.38
Maximum .....	79.97	44.25	31.46	75.91	5.08		0.45
Huckleberry .....	63.02	32.74	24.27	57.01	6.01	0.25	0.28
Lemon .....	64.62	7.31	54.18	61.49	3.13	0.46	0.21
Orange .....	68.56	62.52	3.95	66.47	2.09	0.17	0.30
Peach .....	69.98	56.59	8.75	65.34	4.64	0.24	0.21
Pear .....	69.12	58.46	6.58	65.04	4.08	0.18	0.34
Pineapple .....	80.28	56.70	22.13	78.83	1.45	0.33	0.43
Plum							
Minimum .....	45.56	22.37	19.18	41.85	3.71	1.03	0.40
Maximum .....	73.01	25.48	44.22	66.59	6.42	1.53	0.68
Raspberry							
Minimum .....	63.90	5.07	46.46	58.96	3.94	0.33	0.24
Maximum .....	74.53	21.30	65.52	70.59	6.82	0.84	0.31
Strawberry							
Minimum .....	63.20	17.30	40.83	58.30	5.04	0.25	0.19
Maximum .....	68.11	22.24	44.56	63.56	5.44	0.29	0.21

\* Abnormally high, suggesting gelatine or other foreign matter.

† Alkalinity of total ash = 60 cc.  $N_{10}$  acid.

In these analyses the fruit acidity is calculated in terms of sulfuric acid for convenience in comparing different products. The tendency in recent years has been to cut down the proportion of ordinary sugar (sucrose) used; and with the advent of commercial



pectin preparations there has been more than a tendency to cut down on the proportion of fruit juice used, as remarked above by the Acting Chief of the U. S. Bureau of Chemistry. It would seem that the time was at hand to fix definite minimum limits on both of these items. Recently made jellies will test distinctly lower in all items than do the above products of twenty years ago, due largely to cost of raw materials and use of commercial pectin preparations.

As to 'glucose jellies' (legalized as such in the Federal food standards) we have the following data (Table 6) on products of earlier years. The extent to which 'glucose' had been substituted for cane or beet sugar, varies considerably.

Table 6. Composition of "Glucose Fruit Jellies."

Fruit	Total Solids	Ordinary Sugar	Reducing Sugars	Total Sugars Percent	"Glucose" (approx.)	Acidity (as $H_2SO_4$ )	Non-sugar Solids
Apple							
Minimum .....	63.19	none	38.13	38.13	20.15	0.46	7.30
Maximum .....	65.57	17.76	40.25	58.27	77.00	0.61	27.44
Currant .....	71.86	17.24	37.66	54.90	30.10	0.42	16.96
Grape							
Minimum .....	61.87	1.50	33.93	35.43	8.00	0.45	8.30
Maximum .....	62.02	9.37	44.35	53.72	63.00	0.62	26.44
Guava .....	78.57	32.09	36.32	68.41	6.00	0.45	10.36
Lemon .....	61.03	none	30.16	30.16	70.00	0.61	30.87
Plum .....	66.58	none	37.02	37.02	65.00	0.90	29.96
Quince							
Minimum .....	59.27	none	32.45	32.45	2.00	0.13	7.94
Maximum .....	65.92	17.01	34.91	51.57	66.00	0.17	28.37
Raspberry							
Minimum .....	62.80	none	32.53	33.58	45.50	0.21	24.29
Maximum .....	72.67	1.20	46.13	47.33	68.00	0.24	29.39
Strawberry .....	61.70	3.73	47.84	51.57	10.00	0.67	10.13

Jellies have been variously adulterated at times by other than the above-mentioned methods. Gelatine and agar-agar and other thickening agents have been used, coal-tar colors used to reinforce deficient natural color, and saccharin used as a sweetening agent. Preservatives, which are not needed in properly made fruit jellies, have been used, possibly coming sometimes from fruit juices thus preserved.

#### FRUIT JAMS, MARMALADES, PRESERVES, ETC.

In preceding paragraphs we considered the products (jellies) prepared by mixing the water-soluble constituents of fruits (as fruit juices) with sugar and evaporating to the jellying point. In jams and marmalades more or less of the insoluble matter is included. In jams the whole fruit in small pieces is cooked with sugar and, if

necessary, mashed through a coarse sieve to separate skins, seeds and core particles; in marmalades the whole fruit is pared (if necessary) and cores or pits removed and cooked in small pieces with the sugar, usually to a thicker product than jam. In orange marmalade slices of the fruit are purposely left intact and make an attractive, distinctive product.

As most of the constituents of fruits are in solution (as fruit juice), the composition of jams and marmalades is very similar to that of jellies, but the consistency aimed for in the former is that of a paste that will spread, whereas jellies are more gelatinous and solid. The insoluble portions discarded in jelly making have little nutritive value, but serve to give a more pastelike consistency to the jam or marmalade.

The Federal standard for jam and preserve (see Food Inspection Decision 203, Office of Secretary, U. S. Dept. of Agriculture) is as follows: "Preserve, fruit preserve, jam, fruit jam, is the clean, sound product made by cooking to a suitable consistency properly prepared fresh fruit, 'cold-pack' fruit, canned fruit, or a mixture of two or all of these, with sugar (sucrose) or with sugar and water. In its preparation not less than forty-five (45) pounds of fruit are used to each fifty-five (55) pounds of sugar (sucrose)." "Glucose fruit jam, glucose fruit preserve" is jam or preserve in which a glucose product is used in place of sugar (sucrose).

In addition to standards for jam, preserve and jellies the U. S. Department of Agriculture has fixed standards for fruit butters as follows: "Fruit butter is the sound product made from fruit juice and clean, sound, properly matured and prepared fruit, evaporated to a semi-solid mass of homogeneous consistency, with or without the additions of sugar and spices or vinegar, and conforms in name to the fruit used in its preparation." "Glucose fruit butter" is fruit butter in which a glucose product is used in place of sugar (sucrose). Fruit butter is not standardized as concerns the proportion of fruit and sugar used, as are jam and marmalade. As a rule no sugar is added except with sour fruit, the butter being mainly a boiled-down fruit juice containing some of the pulp, and usually some vinegar. We quote some analyses later.

Regarding the legal requirement of forty-five (45) pounds of fruit to fifty-five (55) pounds of sugar in the preparation of jams or marmalade, there is considerable tendency on the part of many manufacturers to shade this to a 50-50 mixture, which is not so serious

a matter as the recent custom of others to cut the proportion of fruit used down to 35 pounds to 65 pounds of sugar.

The use of commercial pectin aids in this procedure and, as we quoted from the latest U. S. Bureau of Chemistry pronouncement in the section on fruit jellies, a great many products have been found on the market containing only 10 to 20 per cent of fruit. If artificial color is used the Bureau of Chemistry has regarded such products as imitation jams and subject to the legal requirements for the labeling of imitations generally. If artificial color is not used the Bureau has not objected to the sale of these sub-standard products as "Pectin, Sugar and Raspberry (or other fruit) jam."

If the amount of fruit present plus the amount of sugar that would normally be associated with it when prepared into a jam, exceeds 50 percent of the finished product, the Bureau of Chemistry has not objected to a rephrasing in the order of precedence in the labeling, as for example: "Raspberry (or other fruit) jam, sugar and pectin." In all these types of labeling all the words must be set forth in equal prominence, and where acid is added in preparation of these articles an appropriate declaration of that fact must also be made.

The above rules also apply to fruit preserves, which are defined the same as jam. "Citrus fruit marmalade" is legally defined as "the clean, sound, jelly-like product made from the properly prepared juice and peel, with or without the pulp, of fresh citrus fruit, of canned citrus fruit, or of a mixture of these, by cooking with water and sugar (sucrose). It contains, embedded in the mass, pieces of the fruit peel, with or without portions of the pulp of the fruit."

A "preserve" is necessarily a thinner product than jam or marmalade inasmuch as the 55 percent of sugar is dissolved in water to form a syrup, nor is any standard fixed as to the strength of the syrup to be used. However, 45 percent of fruit must have been used. "Bar le Duc" currants, sometimes incorrectly called "Bar le Duc jelly," is a good example of a preserve in which the whole fruit is preserved in a thick syrup and presenting a rather attractive appearance. In preserves generally an attempt is made to preserve the shape of the fruit more or less intact, whereas in jams, marmalades and butters a mashing of the fruit to greater or less degree is practised in order to get a more paste-like product.

A somewhat common method of adulterating jams, aside from the substitution of cheaper fruits like apples, is the utilization of the pulp left in the manufacture of fruit juices and jellies. This pulp is cooked with sugar or glucose, adding acid if necessary and even

Table 7. Composition of Jams and Marmalades

Fruit		Total Solids	Ordinary Sugar	Reducing Sugars	Total Sugars	Non-Sugar Solids (as H <sub>2</sub> SO <sub>4</sub> )	Acidity	Insol. Solids	Ash
		Percent							
Apple									
Minimum	.....	63.22	28.95	25.52	54.63	8.59	0.28		0.20
Maximum	.....	70.12	29.11	31.61	60.24	9.90	0.37		0.31
Apricot									
Minimum	.....	66.06	23.00	34.10	60.42	4.04	0.35	0.88	0.30
Maximum	.....	70.15	29.02	38.96	64.96	5.19	0.41	1.72	0.35
Blackberry									
Minimum	.....	55.42	29.00	18.77	47.77	7.65	0.85	1.96	0.48
Maximum	.....	73.11	33.40	30.46	63.86	9.25	0.96	2.11	0.55
Currant (Black)									
Minimum	.....	55.14	4.14	40.60	47.14	6.10		2.08	0.25
Maximum	.....	75.90	26.40	43.00	68.05	16.07*		14.28*	0.53
Currant (Red)									
Minimum	.....	66.32	1.64	27.86	54.09	5.73	0.43	0.98	0.12
Maximum	.....	72.42	26.23	58.52	65.87	12.23*	1.11	10.47*	0.84
Fig Marmalade	....	69.00	37.90	20.06	57.96	11.04		6.28	0.19
Gooseberry									
Minimum	.....	66.86	6.33	34.90	58.70	3.65		1.26	
Maximum	.....	70.25	31.90	54.80	66.80	8.37		5.35	
Grape									
Minimum	.....	56.64	3.70	33.44	44.77	8.04	0.70		0.19
Maximum	.....	61.80	11.33	50.06	53.76	11.87	0.74		0.48
Grape Marmalade	...	63.01	4.70	48.25	52.95	10.06	0.81	6.61	0.50
Grapefruit Marmalade		69.20	35.51	27.00	62.51	6.69	0.39	1.25	0.33
Guava									
Minimum	.....	70.97	21.27	25.14	64.83	4.62	0.30	1.04	0.30
Maximum	.....	82.46	52.73	43.56	77.87	6.15	0.44	3.30	0.33
Lemon Marmalade	..	67.92	7.00	56.92	63.92	4.00		3.37	
Orange Marmalade									
Minimum	.....	53.87	2.09	13.61	48.15	3.55	0.21	0.09	0.14
Maximum	.....	87.06	54.23	66.26	75.02	12.68*	0.52	6.88	0.44
Pear									
Minimum	.....	61.52	20.28	13.20	46.94	5.45	0.31	1.00	0.28
Maximum	.....	76.33	33.74	50.60	70.88	14.58	0.39	1.72	0.35
Peach									
Minimum	.....	54.90	15.08	15.00	40.60	5.47	0.26	1.08	0.27
Maximum	.....	77.67	53.50	46.78	67.92	14.30*	0.50	7.30*	0.39
Pineapple									
Minimum	.....	55.08	13.90	14.05	47.10	7.98	0.26	5.32	0.24
Maximum	.....	73.92	46.40	33.20	60.45	13.47*	0.31	7.67*	0.30
Pineapple Marmalade		75.57	40.20	31.90	72.10	3.47	0.34	2.62	0.35
Plum									
Minimum	.....	50.43	0.30	22.90	36.80	2.74	0.80	0.79	0.32
Maximum	.....	73.50	36.56	53.90	70.76	25.20*	1.35	10.50*	0.60
Plum (Green Gage)									
Minimum	.....	62.93	5.30	37.01	42.31	3.55	0.39	0.96	0.25
Maximum	.....	74.95	30.68	50.34	71.40	20.62*	0.50	4.93	0.31
Raspberry									
Minimum	.....	46.13	0.50	15.95	30.20	7.18	0.20	2.64	0.18
Maximum	.....	79.40	33.20	54.57	73.20	25.20†	0.61	13.57*	0.35
Strawberry									
Minimum	.....	38.40	3.70	8.30	36.50	2.00	0.48	1.52	0.25
Maximum	.....	75.83	48.17	61.61	72.64	18.39	0.53	7.48	0.42

\* Includes pits or seeds or pieces of skin, as of orange.

† One sample showed 50.16 percent indicating use of raspberry pomace entirely.

Table 8. Composition of Fruit Preserves

Fruit	Total Solids	Ordinary Sugar	Reducing Sugar	Total Sugars	Insol. Solids	Acidity (as $H_2SO_4$ )	Ash	Solids (in Syrup)
	Percent							
Apricots .....	65.50	25.32	23.13	48.45	17.05	0.88	0.48	71.85
Blackberries .....	28.97	none	23.30	23.30	4.72	0.49	0.45	
Cherries								
Minimum .....	50.88	1.88	35.23	47.90	3.00	0.15	0.19	46.01
Maximum .....	70.82	22.70	46.00	57.93	12.89	0.82	0.36	68.86
Cranberry .....	46.93	0.22	41.20	41.44	2.68	(Sugar free)	solids=5.49	
Currant (Bar le Duc)	70.90	9.87	54.54	64.41	0.99	0.45	0.14	
Strawberry								
Minimum .....	31.86	0.46	15.95	29.73	2.00	0.24	0.17	
Maximum .....	68.82	22.90	52.13	58.80	7.07	0.56	0.38	

artificial flavor and color. The product, however, will be deficient in constituents characteristic of the fruit juice. The substitution of cheaper fruits (apple for instance) is revealed by a chemical study of the fruit acids present and a microscopical study of cell fragments and other tissues and seeds. In U. S. Bureau of Chemistry, Bulletin 66 will be found an excellent microscopical study of the tissues of various fruits, accompanied with careful illustrations.

Regarding the chemical composition of different fruit jams, marmalades and preserves, the various state and government reports do not differentiate as often or as well as they might, there being a tendency to class all three together simply as "jams." The preceding data are for jams unless specified otherwise. Acidity is expressed in terms of sulfuric acid ( $H_2SO_4$ ) rather than in terms of the actual fruit acids present, for convenience in making comparisons. Inasmuch as jellification is not looked for in jams, marmalades and preserves, the degree of acidity and proportion of pectin are not such important factors as in jellies. However, a jam must not be too acid to be palatable, and pectin, as we have alluded to, is used considerably in obtaining desirable consistency, especially when less than the legal proportion of fruit has been used.

Many of the jam products reported were imported from England, where the art of making high grade jams and marmalades has reached a point near to perfection. Jam and marmalade are much more common articles of food in England and the English colonies than is the case here.

Preserves, as we have said earlier, are of a thinner consistency than jams and marmalades and an effort is made to keep the fruit intact. Fruits canned in a thin syrup depend entirely upon hermetical sealing for preservation, but when put up in a sufficiently thick syrup, they are preserved more or less by the sugars present. In the

above analyses we have included products sometimes referred to as "canned fruits," which, having been put up in a thick sugar syrup, may also be classed as "preserves."

The composition of the "glucose jams, marmalades and preserves" bears practically the same relation to the above analyses that the "glucose jellies" (see preceding section) bear to the regular fruit jellies, the principal difference being the presence of a small percentage of "insoluble solids" coming from the inclusion of cell-wall tissues and seeds.

The "fruit butters," referred to above, in connection with the legal standards, have not been analyzed to any degree, except in the case of "apple butter."

Table 9. Composition of Apple Butter.

	<i>Total Solids</i>	<i>Ordinary Sugar</i>	<i>Reducing Sugars</i>	<i>Total Sugars</i>	<i>Non-Sugar Solids</i>	<i>Acidity (as <math>H_2SO_4</math>)</i>	<i>Ash</i>
	Percent						
Minimum .....	47.42	0.75	37.20	38.34	6.48	0.40	0.70
Maximum .....	47.91	1.14	40.68	41.43	9.08	0.44	0.97

The apple butters shown in Table 9 were evidently made without vinegar, as the acidity corresponds to that of sweet apple juice boiled down to a similar consistency. Any sugar, if added, would be largely converted into reducing sugars by the long continued boiling in the presence of fruit acid. The data on the above samples indicate that no sugar was used.

### CANNED FRUITS

"Canned fruit" is legally defined as "the clean, sound product made from properly prepared fresh fruit, with or without water and/or sugar (sucrose), (a) by processing in a suitable hermetically-sealed container, or (b) by heating or packing in a suitable container which is then hermetically sealed."

As yet, the Federal food inspection officials have done very little in grading canned fruits, but in California a law has recently been proposed that all fruits canned, which are not suitable for the "Fancy," "Choice" and "Standard" grades hitherto in use by the trade (particularly the "Canners League of California"), shall be labeled "Seconds" on the top of the can. Five grades are being packed at present; but as yet the distinctions are not exact enough to serve in food inspection for the guidance of judges, juries and consumers.

The information concerning the chemical composition of canned fruits is not entirely satisfactory. Certain local associations have

attempted to standardize the sugar strength of the syrups used in canned fruits and below we give data on the sugar content of syrups in canned fruits, as found on analysis. The Bulletin 66 data did not report the percent of solids both in the whole product and in the syrup also in any case, but in most of the samples (75 in number) the percent of solids in the syrup was determined and we will quote that mainly. The solids in the syrup would be principally sugar, hence the figure given in each case may be regarded as the sugar strength of the syrups used with different fruits. The data (Table 10) are somewhat old, but still apply, as present-day standards have not greatly improved.

Table 10. Analyses of Canned Fruits.

	<i>Total Solids in Can</i>	<i>Total Solids in Syrup</i>	<i>Acidity (as H<sub>2</sub>SO<sub>4</sub>)</i>	<i>Reducing Sugar Percent</i>	<i>Sucrose</i>	<i>Total Ash</i>	<i>Alkalinity (as K<sub>2</sub>CO<sub>3</sub>)</i>
Apples .....	....	8.17	....	....	....	0.147	0.115
Apricots							
Minimum .....	....	16.84	0.88	....	0.59	0.345	0.170
Maximum .....	....	71.87	....	....	25.32	0.479	0.344
Blackberries .....	....	28.20	....	....	....	0.423	0.192
Blueberries .....	....	12.18	....	....	....	0.166	0.134
Cherries							
Minimum .....	24.81	12.23	0.05	....	0.00	0.045	0.017
Maximum .....	70.82	68.86	0.82	....	22.70	0.408	0.311
Figs							
Minimum .....	....	56.98	0.09	....	23.83	0.131	0.081
Maximum .....	....	63.53	....	....	41.34	0.236	0.199
Orange .....	....	62.70	....	....	15.00	0.468	0.245
Pineapples							
Minimum .....	....	20.79	0.51	....	0.00	0.059	0.050
Maximum .....	....	59.94	0.56	....	17.45	0.629	0.457
Plums							
Minimum .....	21.90	26.99	0.60	....	0.23	0.156	0.104
Maximum .....	26.74	41.07	0.77	....	6.46	0.281	0.215
Peaches							
Minimum .....	....	16.78	0.30	....	0.68	0.253	0.171
Maximum .....	....	27.20	0.48	....	46.40	0.351	0.268
Pears							
Minimum .....	14.10	8.95	0.11	....	0.37	0.081	0.052
Maximum .....	31.86	60.94	0.16	....	27.26	0.230	0.183
Raspberries							
Minimum .....	34.36	....	0.20	....	0.60	0.279	0.206
Maximum .....	69.12	37.53	0.66	45.76	3.34	0.308	0.280
Strawberries							
Minimum .....	31.86	....	0.20	29.28	0.60	0.169	0.099
Maximum .....	71.76	....	0.56	52.13	19.08	0.356	0.250

The data show a very wide range of practice in the strength of syrup used in canned fruits; also in the degree of inversion of the sugar (sucrose) there is a considerable variation, due to different acidities and length of processing. To get the "total sugar" one

adds the "reducing sugar" to the sucrose and in many cases where the "reducing sugars" were not determined, it is permissible to assume that about 90 percent of the difference between the total solids and the sucrose represents the "reducing sugar."

The data on the ash and alkalinity of the same are of value in detecting the canning of extracted fruit, as the sugar used in the syrup would furnish practically no ash (mineral residue).

There is obviously a need of standardizing the strength of syrup used in canning fruits and the action of the "Canners League of California" along this line is meritorious.

### COMMERCIAL MATURITY OF FRUITS

Once upon a time all people ate fruits as they came from the tree, bush or vine, and ate them ripe, with a flavor that nature only can impart. But with the development of the commercial fruit growing business, as concentrated in certain sections, and the resulting necessity of shipping long distances by relatively slow means of transportation, a new condition of affairs has come about and many people, especially in the big cities, have little or no idea of the natural flavor of certain fruits. For instance a tomato ripened on the vine bears only a morphological resemblance to the more or less tasteless tomato, picked green and allowed to turn partially red before being sold. It has the same form but the flavor and other things dependent upon natural ripening, have but slight resemblance. The same can be said of bananas, oranges, watermelons and other melons, and several other fruits.

In order to ship some of these fruits to the market, it is of course necessary to pick them before they are fully ripe, but in the race to get shipments to the markets ahead of other growers, to deliver fruits out of season, and to enable careless packing, a flagrant abuse has grown up. Fruits have been picked and shipped when very immature, color has been developed by artificial means (heat and sweating) and other tricks resorted to, none of which helped to develop a liking for the fruit among the consumers.

Finally the abuses became so flagrant and widespread that the provisions of the Federal Food Law referring to misbranding and technical adulteration were invoked by food inspection officials and prosecutions of fruit shippers resulted.

It was realized by these food inspection officials, however, that a new degree of maturity must be studied as a standard; that full



maturity due to ripening on the tree, bush or vine was a commercial impossibility in many cases and that an intermediate point between utter greenness (immaturity) and full maturity must be considered. This intermediate point is being called "commercial maturity" or that degree of maturity which will stand long shipment and yet result in the sale of products which are technically ripe, though of different flavor than fruits that have ripened on the plant bearing them.

Some of these studies, which are necessarily of a technical nature, have been completed and standards fixed, others are under way, especially in the U. S. Department of Agriculture, to which such an investigation belongs by virtue of its position as a governmental aid to fruit growers and as a defender of the consumers against fraud under the Federal food law. In the case of oranges and grapefruit, the food inspection officials of Florida, especially Dr. R. E. Rose, the State Chemist, investigated and assisted greatly, with the co-operation of the more thoughtful growers and shippers, who realized what harm might result to their industry if the abuses remained unchecked. State standards and Federal standards have resulted and simple tests devised by which the orange and grapefruit growers and shippers can determine when the fruit is ready for picking to yield a product technically ripe upon arrival at the market point.

Thus oranges and grapefruits must not be found in interstate commerce unless they comply with the Federal standards.

The full "ripening point" may be considered as that point where the sugar content of unpicked fruit reaches the maximum. The "commercial maturity" considers the fact that full ripening is not always practicable and a point is fixed that will yield an acceptable product to the distant consumer.

In Bulletin 94 of the U. S. Bureau of Chemistry the results of studies on the ripening of apples of different varieties are given, also changes taking place during storage, but as yet there has been no legal definition of "commercial maturity" for that fruit.

More recently has appeared Bulletin 1250 of the U. S. Department of Agriculture, entitled the "Relation Between the Composition of California Cantaloupes and their Commercial Maturity." With the usual methods of handling, if melons have been allowed to develop too far before picking, they can be shipped only short distances and are sold in nearby California cities as "choice." For eastern shipments of from 2,000 to 3,000 miles it has been customary to pick melons before any trace of yellow color has developed. This has resulted in the picking of melons which are too green, and these

reached the consumers in a tough, shriveled condition, lacking in color and flavor. The shipment of such green melons is a quick way to ruin the demand and the purpose of the investigation reported in Bulletin 1250 was to devise suitable tests by which the state of development of cantaloupes can be judged and by means of which growers and shippers may be sure that mature melons are selected and the too green ones left on the vine. Information as to the changes taking place in the composition of the melons after picking was also looked for in order to determine whether their composition at the time they are sold to the consumer is an indication of condition at time of picking.

It was necessary, therefore, to study the composition of the fruit at different stages of maturity to ascertain, if possible, what relation existed between the eating quality of the fruit and its composition; and to determine to what extent the external appearance can be correlated with the internal condition. From these relations a limit below which melons could be regarded as unsuitable for marketing could be fixed.

This investigation might be considered as a general working outline for any fruit and a study of the bulletin is well worth while. In addition to cantaloupes, data are reported on "Eden Gem Melons," Early Watermelons and Honeydew Melons. The summary of results on cantaloupes is that the soluble solids, refractive index of the juice and its sugar (sucrose) content increase as the melons ripen and the percentages of starch in the seeds decreases. The juice of melons which are sufficiently mature when picked has a specific gravity of at least 1.040, equivalent to 10 percent of solids (soluble), a refractive index of at least 55 in an immersion refractometer and a sugar (sucrose) content of at least 4.5 percent. The seeds of such melons contain less than 0.5 percent starch. Melons gain in flavor, but not in sweetness, after being picked. On storage at low temperatures such as are found in iced cars the melons change but little chemically, so that their condition during and immediately after storage indicates their condition when picked.

Undoubtedly official standards will be issued governing the "commercial maturity" of these melons and in time we shall have similar standards governing the maturity of all fruits which are necessarily picked before the condition of full maturity, due to commercial requirements, especially long distance shipping.

## SUGARS IN JELLIES\* AND JAMS

According to circumstances, there are four sugars that may be found in jellies and jams. Most fruits contain three sugars which make up the greater part of the total solids of the fruit, or the juice expressed therefrom. The commonest sugars in fruits are the two "reducing sugars" (so-called because they reduce an alkaline copper salt solution to the red oxide of copper) known as levulose and dextrose. Levulose is the principal sugar of the apple (about 6 percent) while the principal sugar of the grape is dextrose. The apple, however, contains dextrose and the grape also contains levulose and most of the other fruits contain approximately equal proportions of these two so-called "fruit sugars," or, as called above, "reducing sugars." The third sugar found in fruits is sucrose, of which cane sugar, beet sugar and maple sugar are familiar examples.

Some fruits, the peach particularly, are relatively rich in sucrose. The apple contains about 4 percent (about one-fourth of the total solids of the apple) and some grapes contain considerable sucrose also. During alcoholic fermentation, sucrose first and quickly disappears, then dextrose and finally most of the levulose.

Thus in a fruit we may have three kinds of sugar present. The sucrose added, in the form of cane sugar or beet sugar, to a jam or jelly can not be differentiated from any sucrose naturally present in the fruit used. However, the sucrose coming from the fruit is a quite small proportion in a jelly or a jam made with 45 percent of fruit (containing from 85 to 90 percent fruit water) and 55 percent sucrose (cane or beet sugar), as called for in the legal standards. The bulk of the fruit sugars present will be levulose and dextrose.

When sucrose (cane sugar, for instance) is heated in the presence of fruit acids, as is the case in jelly and jam manufacture, the sucrose is more or less decomposed ("inverted") into equal parts of levulose and dextrose (known together as "invert sugar") and thus it is that in a jelly or jam made with 50 to 55 percent of sucrose, upon analysis we may find only 10, 20, 25 or 30 percent of sucrose as such, and the "reducing sugars" (levulose and dextrose, classed together as "invert sugar") much more than the 45 percent of fruit would furnish.

In analysis, the sum of the unaltered sucrose and the reducing sugars (usually reported in terms of "invert sugar") is reported as the "total sugars," which, subtracted from the total solids, gives us

\* See appendix for abstract of Bulletin by Tarr and Baker of the University of Delaware Experiment Station, on effect of sugar in jelly manufacture.

the item known as "non-sugar solids." By appropriate formulae, the "sucrose originally present" can be calculated and from a study of the percentages of non-sugar solids, soluble and insoluble solids, fruit acid, ash (residue from mineral salts of fruits) and alkalinity of the ash, an approximately correct estimation of the percentage of fruit originally present can be made. The item "insoluble solids" (absent of course in a clear jelly) comprises the cell-wall substances of the fruit and any seeds or skin tissue.

A moderate degree of this altering of sucrose into invert sugar (equal parts of levulose and dextrose) by heating with the acid of the fruit is desirable, as it prevents crystallization, invert sugar being non-crystallizable; but too great an inversion gives a poor jelly or jam, one that is too fluid or in which the water of the jelly later separates. A good rule is to add the sucrose (cane or beet sugar) during the last half of the cooking, thus avoiding too much inversion into invert (reducing) sugar. Sucrose does not reduce an alkaline copper salt solution and is therefore not a reducing sugar, like levulose and dextrose.

The Federal standard for legal products calls for the use of at least 45 percent fruit to 55 percent sucrose. If sucrose is first dissolved to a thick syrup, evaporation must be allowed during cooking to compensate for this added water, of course. Thus, before adding the sugar syrup, the fruit juice or pulp could be boiled down, so that the loss of water exactly equaled the water added to the sugar. Then the 45-55 ratio would be preserved with perhaps less shrinkage of the finished batch. Considerable would depend upon the amount and quality of the natural pectin present. If the latter were deficient, a little concentrated (dry) pectin might be necessary, which under present rules, however, would have to be admitted on the label. If the product is noticeably substandard with respect to percent of fruit present, then such a use of pectin would result in its legal classification as a "Pectin (Fruit) Jelly" (or Jam). Pectin-sugar preparations in which just enough fruit is present to give a slight flavor must be labeled as "Imitation," as said before.

The fourth sugar that may be present in jellies and jams is commercial glucose, a mixture of water, gum dextrin and dextrose, resulting from heating starch paste with a trace of mineral acid. In Europe this is known as "starch syrup" or "starch sugar" (according to concentration) and has been called "corn syrup" here when made from corn starch paste. Such jellies and jams must be labeled as "glucose jelly" (or jam). For diabetic patients, a writer has re-

cently suggested jellies and jams made from fruit, pectin and saccharin. Ordinarily saccharin (an organic chemical some 500 times sweeter than sucrose) is not allowed in food products. It has no food value, being merely a sweetening agent.

#### PECTIN CONTENT OF CERTAIN FRUIT PRODUCTS

At a recent convention of preserve manufacturers, complaint was made against the chemical profession, on account of the scarcity of good data on the pectin content of various fruits and fruit products. There are some published data in a widely scattered form and many more unpublished data in the possession of the experts of the U. S. Bureau of Chemistry. Possibly the latter will be published in due time and it would appear that, if trade associations are interested in the matter, they should finance such an investigation themselves or else persuade the Bureau of Chemistry to publish data now already available. Such an investigation is a long affair and consulting chemists can not be expected to carry it out as a "labor of love" and even an association chemist would have to devote most of his time for many months to such a study.

The writer has access to some data, however, that may prove of interest. The commonest method of estimating pectin is by precipitating by an excess of strong alcohol and under the term "alcohol precipitate" there are a number of published analyses of fruits and juices, etc., which report the pectin thus, notably Bulletin No. 66 of the U. S. Bureau of Chemistry.

C. A. Browne, in his exhaustive analysis of the apple and its products, reported 0.4 percent as the average pectin content of that fruit, the range being from 0.2 to 0.6.

Table 11 gives the figures reported in Bulletin No. 66 and will give some idea of the range in different fruits and fruit juices and jellies and jams.

The products were all of known purity and strength and were made long before the use of commercial pectin preparations was heard of. There seems to be no logical reason why an addition of a tiny percentage of pectin to a fruit produce deficient in natural pectin (or a batch of an expensive pure fruit product, which for some reason doesn't jell or thicken up well) should be proscribed in any way, so long as the product is not substandard in any way, so long as no fraud is concealed thereby.

Because the use of pectin has been abused (substituted for fruit

Table 11. Range of Pectin Content of Fruits and Fruit Juices, Jams and Jellies.

	<i>Minimum</i>	<i>Maximum</i> Percent	<i>Average</i>
Blackberry (Fruit) .....	0.61	0.74	0.68
Cherry (Fruit) .....	...	...	0.67
Currant (Fruit) .....	...	...	0.80
Red Raspberry (Fruit) .....	0.70	0.78	0.74
Strawberry (Fruit) .....	0.48	0.56	0.51
Black Raspberry (Juice) .....	1.00	1.62	1.31
Red Raspberry (Juice) .....	0.65	0.73	0.69
Strawberry (Juice) .....	0.48	0.69	0.56
Apple (Jelly) .....	0.81	1.30	1.08
Currant (Jelly) .....	1.18	3.36	2.10
Grape (Jelly) .....	1.25	2.49	1.87
Guava (Jelly) .....	1.36	1.59	1.47
Lemon (Jelly) .....	...	...	0.73
Strawberry (Jelly) .....	0.89	1.47	1.18
Raspberry (Jelly) .....	0.77	1.45	1.11
Apricot (Jam) .....	...	...	1.14
Currant (Jam) .....	...	...	0.92
Orange (Jam) .....	0.54	1.76	1.24
Peach (Jam) .....	...	...	1.49
Plum (Jam) .....	1.09	1.63	1.36
Strawberry (Jam) .....	...	...	0.90

or sugar which should be present), it has gotten a reputation somewhat akin to commercial glucose, and to require a statement on the label when a possible fraction of one percent has been added to a batch of good grade, legally pure jelly or jam, seems rather hard on the trade.

There is considerable need of more data on the exact proportion of pectin in fruit products, in order to judge whether pectin is needed to get a perfect jelly. It is rather absurd, when various official agencies (State Agricultural Experiment Stations, etc.), are carrying on studies in jelly making and publishing the pectin, sugar and other limits necessary to get good jellies, etc., that another official agency (the U. S. Dept. of Agriculture) should be making labeling requirements on standard products, which tend to discourage scientific jelly making. Of course, when pectin conceals fraud or substandard conditions, strict labeling requirements are desirable.

#### CITRUS AND APPLE PECTINS

The principal source of commercial pectin, so far, has been the apple pomace left from the manufacture of cider and cider vinegar. And it has been a very satisfactory raw material for the manufacture of pectin, as it is a cheap by-product or even considered as actual refuse in earlier times, to be disposed of at some cost of labor.

It is satisfactory also because the yield of pectin is fairly high and of good grade, having no disagreeable taste and having good jellying value. However, there are many other sources of pectin in nature and some of them are likewise by-products, hitherto considered as waste material. The growth of the orange juice beverage industry and also by-products from lemons and grapefruit have furnished large quantities of citrus peel and pulp, which somewhat recent investigations have shown to be quite rich in pectin of good jellying power, albeit it has a bitter taste rather hard to remove.

A quite thorough investigation of the manufacture and properties of citrus pectins has been published by the United States Department of Agriculture as Department Bulletin No. 1323, by Dr. Homer D. Poore of the Bureau of Chemistry. In this investigation, the properties of citrus fruit pectins were studied and methods of production compared.

The best method of extracting the pectin was to heat the finely ground peel or other citrus by-product with acidified water\* and clarify the pressed out extract with kieselguhr. A powdered pectin preparation was prepared by the spraying process from this extract (after concentration by freezing out water) and analyzed as shown in Table 12.

Table 12. Powdered Citrus Pectin

	Percent
Moisture .....	3.62
Acidity (as citric acid) .....	6.75
Pectin .....	43.70
Proteins .....	5.28
Ash (mineral residue) .....	9.14
Sugars .....	trace

This powdered preparation was very bitter and gave a bitter taste to jellies in any proportion used. By washing sufficiently with strong alcohol, the bitter taste can be removed, but it is not a commercially practical proposition. The process of most promise consists of concentrating the extract to a paste, meanwhile washing by a continuous system with a minimum quantity of denatured alcohol. A standard jelly test for determining the quality of various pectins was developed and the proportions of citric acid, sugar and citrus pectin required to give good jellies were determined. The minimum limits to give good jellies were, citric acid, 0.045 percent, citrus pectin 0.20 percent, and sugar (sucrose), 37 percent.

Samples of dried lemon, orange and apple pectins were prepared

\* Rooker advises 0.2 percent lactic acid solution.

and compared chemically for the purpose of distinguishing between them. As will be seen (Table 13) no decided differences were found and no hope is held out of being able to differentiate them chemically.

Table 13. Composition of Pectins.

	<i>Apple</i>	<i>Lemon</i> Percent	<i>Orange</i>
Moisture .....	1.12	3.64	8.14
Ash (mineral salts) .....	0.70	5.42	5.90
Alcohol ppt. (pectin) .....	96.72	89.90	81.76
Methoxy Number .....	10.90	10.26	8.85
Specific rotation .....	+ 210.0°	+ 206.5°	+ 175.0°

When calculated to the basis of alcohol precipitate (pure pectin) the differences between the methoxy numbers, specific rotation, sodium hydrate required for cold hydrolysis, pectic acid yield and yields of araban and galactan were all very slight, suggesting that citrus pectin and pectin from apples are identical in chemical constitution.

Presumably pectin prepared from apple by-products, particularly pomace, will continue to be the one most in use, but it is interesting to note, however, that other waste products of the fruit industry can be utilized and that citrus pectin, free from bitter flavor, is a commercially practical proposition, giving good results in jelly making and being evidently of exactly the same chemical constitution as apple pectin. It would be of interest similarly to investigate the by-products (skins, etc.) of the grape juice industry.



## Chapter II.

### The Legal Chemistry of Vinegars.\*

#### VINEGAR IN GENERAL

The use of vinegar for condimental purposes, particularly wine (grape) vinegar, is very ancient, possibly being contemporaneous with the utilization of wine itself. Practically any fruit juice capable of alcoholic fermentation can be converted into a vinegar by a subsequent acetic fermentation, which is also true of weak sugar syrups and solutions of honey. Moreover, of course, the weak alcoholic beverage obtained by fermentation of a malt beer wort (before the addition of hops) can be submitted to acetification to produce malt vinegar; and a weak alcoholic spirit ("low wine") distilled from a suitable fermented "mash" can likewise be submitted to an acetic fermentation, furnishing the so-called "distilled" or "spirit" or "grain" vinegar.

Vinegar is essentially a dilute solution of acetic acid, but it must be remembered that it is the product of a definite fermentation, containing appreciable quantities of certain solid and liquid substances derived from the material thus fermented, and that a solution of commercial acetic acid (as purchased in the chemical markets) reduced to proper strength can only be considered as an "imitation spirit vinegar" at the best, and as an imitation of a good spirit vinegar it would be a very poor makeshift.

The constituents other than acetic acid which are present, as well as the characteristic flavor, etc., of a true vinegar, depend of course upon the nature of the material which has been fermented into vinegar. The four principal vinegars in use at present are: wine vinegar, resulting from the alcoholic and subsequent acetic fermentation of grape juice; cider or apple vinegar, from properly fermented pure apple cider; malt vinegar, from the alcoholic and subsequent acetic fermentation of an undistilled infusion ("wort") of barley malt, or cereals whose starch has been converted into sugar by use of malt; and spirit vinegar as mentioned above. A "dried apple vinegar" of

\* Originally published in *The American Vinegar Industry and Fruit Products Journal*, Aug., 1922, *et seq.* as a revision of articles appearing earlier in *The Spice Mill*.

excellent quality can be made by extracting the sugars, etc., from dried apple products and properly fermenting the infusion thus obtained, very similarly to making a raisin wine from certain varieties of dried grapes.

In addition there is more or less manufacture and sale of a sugar or syrup vinegar made from the alcoholic and subsequent acetic fermentation of solutions of syrup molasses, etc.; glucose vinegar from similarly fermented glucose solutions; honey vinegar from fermented honey solutions; and special fruit vinegars. Vinegars are now being made from the juice of pears, watermelons, oranges, raspberries and water extract of prunes.

In some countries a certain vinegar is often so extensively used, or was so exclusively used originally, as to restrict the simple term "vinegar" to that particular variety as, for example, malt vinegar in England, or wine vinegar in France, Italy, Spain, Greece, etc.; spirit vinegar in Germany. Each has become what might be called the "national vinegar" of that country. In the United States the only vinegar known for years was cider vinegar, and among food inspection officials it has always been customary to hold that when the customer simply asks for "vinegar," cider vinegar is called for and should be furnished by the dealer. Thus the Federal food standards (Circular 136, Office of Secretary, U. S. Dept. of Agriculture) restricts the single term "vinegar" to indicate cider vinegar made from the fresh juice of apples.

The artificial coloring of vinegar is prohibited by many State food laws. It can be readily seen that the coloring of a naturally colorless vinegar, as, for instance, spirit vinegar or glucose vinegar, is for fraudulent purposes only. In vinegar having a color naturally and where the use of added color conceals no adulteration, a more liberal view might be appropriately taken. Thus modern, quick, sanitary methods of handling crushed apples result in a very light-colored cider vinegar. The older, more careless processes resulted in a rich brown color as the standard to be looked for in buying circles. It would seem as though the use of a little burnt-sugar (caramel) coloring should be permissible in such a case, for as it stands now the better vinegar of the two, submitted to a buyer, might be discriminated against, because of a pale brown or yellow color.

Vinegars are subject to more or less deterioration depending upon age, purity and method of storing; it being possible for certain vinegars, in time, not only to lose all their acetic acid, but to become actually alkaline in reaction. This deterioration is due usually to a

destructive fermentation caused apparently by bacteria of the *Bacterium xylinum* type, as a cellulose-containing "mother" is usually formed.

Bertrand (Comptes Rendus, 122,900) states that the well-known vinegar-flies (*drosophila cellaris*) which frequent places where fruit juices are fermenting, introduce the *Bacterium xylinum*. Pasteur claimed that the acetic acid-forming bacteria themselves (*Mycoderma aceti* and *Bacterium Pasteurianum* principally), after converting the alcohol into acetic acid, consume the latter, forming carbon dioxide and water. Other investigators, (see reference in "Chemical Abstracts" Jan. 10, 1912, p. 101-2) have shown that certain molds also destroy acetic acid in vinegars.

Vinegars are frequently found to have increased in acetic acid strength, due to their having been sent out into the market before all the alcohol of the fermented juice or infusion has been fermented into acetic acid. Some State inspection officials withhold a prosecution for low acidity, if there is sufficient alcohol present to ultimately yield the legally required percent of acidity. This is rather absurd, as the purchaser (housewife) wants vinegar for its acidity at time of sale, and not to keep until fermentation is complete.

As is well known, the alcoholic fermentation itself is caused by various species of yeasts (*Eumycetae*) acting on certain reducing sugars through the agency of the ferment or enzyme, known as zymase. This zymase can be isolated from the yeast and used directly to induce alcoholic fermentation in solutions of reducing sugars, for instance levulose and dextrose.

The constituents of a vinegar other than acetic acid which are present vary, as said before, according to the nature of the fermented juice or infusion or distilled spirit from which the vinegar has been made. In distilled or spirit vinegar there is naturally very little solid matter, but in other vinegars, noticeably malt, cider and wine vinegars, the proportion of solids is not only appreciable, but sometimes relatively high. These solid constituents may furnish some of the characteristic flavor of a vinegar, but the principal cause of flavor and odor (aside from that due to acetic acid itself) is the presence of certain fluid constituents of an ester nature, formerly called "ethers". In a well-aged cider vinegar the odor of the ester, known as ethyl acetate, is often quite strong; in fact the author knows of a case where the "vinegar stock," or fermented cider, contained little or no alcohol, no acetic acid, but a considerable quantity of the esters, particularly ethyl acetate.

The greater proportion of all the vinegar sold in this country is made by the so-called "generator process" or "quick process," but there is no denying that a properly conducted cask fermentation, extending over a period of a year or so, furnishes a superior product, particularly as concerns flavor, odor, etc. The use of selected yeast cultures for converting the original fruit juice into an alcoholic liquid, as is the custom in Europe, would no doubt offset some of the disadvantages of the "generator process"; and by a cask fermentation would yield a magnificent product.

In succeeding paragraphs we will take up in turn each of the various vinegars, with especial reference to their chemical make-up, etc., as called for in the Federal food standards; together with some simple chemistry of the changes taking place in the fermentations and the general make-up of the raw materials subjected to fermentation.

#### CIDER OR APPLE VINEGAR

In the Federal food standards as originally issued (Circular 136, Office of Secretary, U. S. Department of Agriculture), "vinegar" is considered as synonymous with "cider vinegar" or "apple vinegar," the "product made by the alcoholic and subsequent acetous fermentation of the juice of apples, is levorotatory, and contains not less than four (4) grams of acetic acid, not less than one and six-tenths (1.6) grams of apple solids, of which not more than fifty percent (50 percent) are reducing sugars, and not less than twenty-five hundredths (0.25) gram of apple ash in one hundred (100) cubic centimeters (20° C.); and the water-soluble ash from one hundred (100) cubic centimeters (20° C.) of the vinegar contains not less than ten (10) milligrams of phosphoric acid ( $P_2O_5$ ), and requires not less than thirty (30) cubic centimeters of decinormal acid to neutralize its alkalinity."

In Food Inspection Decision 193, issued Sept. 15, 1924, this standard was simplified by eliminating all analytical limits except the requirement of "not less than four (4) grams of acetic acid." To the official chemist is left the question of deciding if the definition part of the standard has been complied with, from a study of all data.

The usual State standard in the past has been a very simple requirement of at least a certain acetic acid strength (usually 4.0 or 4.5 percent) and at least a certain proportion of solid residue (varying from 1.5 to 2.0 percent) with very rarely a limit (0.25 percent) for ash (residue left upon properly incinerating the total solids) and a frequent prohibition of any artificial color.

More recently various States have adopted the former Federal standard complete and in the near future this may become universal throughout State food inspection. This standard needs some revision, which will come in due time.

Vinegars are allowed, by regulations issued subsequent to the Federal standard (see Food Inspection Decision 140, U. S. Dept. of Agriculture) to be diluted to standard strength (4 percent); but the label must plainly state the fact. Whether the water is added to the pomace after pressing once, or later in the process, makes no difference, the dilution must be indicated on the label. As dilution would reduce not only acid strength, but all other ingredients and analytical requirements proportionately, as well, diluted vinegars will not be expected to comply with the analytical limits of the old Federal standard, except as concerns the acidity requirement, but, of course, mere dilution will not alter the relations existing between these other analytical items.

Food Inspection Decision 140 also requires that the mixing of vinegars made from different raw materials be indicated on the label by the use of the word "compound," together with the names and proportions of the various ingredients; and products artificially colored or flavored, with harmless substances, in imitation of some particular kind of vinegar may be sold if labeled "Imitation Vinegar."

Concerning "second pressings," the number of pressings used in making the juice is held to be immaterial provided the pomace is fresh or not decomposed by fermentation. Water used at this stage would have to be indicated on the label, as said above, and the use of pressings from fermented pomace comes under the legal definition of "filthy and decomposed material" and can not be used at all.

Food Inspection Decision 140 also provides for vinegar made from dried-apple products (skins, cores and "chops") "by the process of soaking, with subsequent alcoholic and acetic fermentation of the solution thus obtained." It is "not entitled to be called 'vinegar' without further designation, but must be plainly marked to show the material from which it is produced." The dried apple material must, of course, be clean and undecomposed.

The vinegar made from soaking dried "chops" (which are the whole apple) will, of course, be a more complete duplication of cider vinegar, than that made from dried skins and cores, and is appropriately called "dried apple vinegar." In fact, for a short time the term "apple vinegar" alone was permitted for vinegars made from dried apple products, but generally speaking "apple vinegar" is synonymous with "cider vinegar" and the indication on the label as to the condi-

tion of the apple material used is fair and proper and now officially required. During drying the natural flavoring ingredients of the apple are largely lost and other slight changes occur, so that the alcoholic product and the subsequent vinegar are not just the same as cider vinegar, no matter if the usual analysis is the same.

As concerns the old State standards, in the manufacture of cider vinegar, some very shrewd sophistications are practised, both intentionally and unwittingly, and the State standard of the past was utterly useless in detecting or preventing such, as acidity could be easily manipulated by means of commercial acetic acid or strong spirit vinegar and solids and ash could be furnished by almost any non-volatile substance. Even the restrictions of the original Federal standard have been evaded by factory chemists using apple jelly; and mineral salts which would furnish alkalinity and phosphoric acid values to the water-soluble ash; and glycerin for the proportion of that substance which is usually looked for in official analytical work; and other shrewd scientifically guided adulterations. In fact, a complete legal purity analysis of cider vinegar now requires about three times as many items as mentioned in the standard.

This Federal standard (in which grams per 100 cubic centimeters correspond very closely to percentage) was an attempt to fix limits with which only a straight apple (juice) vinegar would comply and, although it is faulty in certain respects, principally in the liberality of the reducing sugar limit, yet only an occasional shrewdly sophisticated sample will pass muster, and such crude adulterations as were possible under old State standards would never pass. This standard has now been adopted in full or in part by a number of State inspection departments, as said above.

The first part of the Federal standard for cider or apple vinegar specifies a product made by certain fermentations of "the juice of apples" and, although many vinegar makers buy an already alcoholic-fermented "vinegar stock," yet others carry through the process from the culture of the apple tree up to the finished product and, as a proper understanding of the Federal cider vinegar standard necessitates studying back as far as the apple juice, we will begin with the apple itself.

The apple (*Pyrus malus*) belongs to the Pome class of fruits, and many different varieties exist. In France, Germany and England the culture of special varieties peculiarly adapted for the manufacture of cider is quite ancient and the utilization of the juice of these varieties in connection with pure cultures of yeasts and a general scientific con-

trol of the process has resulted in a beverage industry rivaling the wine industry itself.

Alwood (Bulletin 71, Bureau of Chemistry, U. S. Dept. of Agriculture) has carefully studied the cider industry in England and continental Europe and his observations lead us to believe that although our grape juice industry is fairly well developed, we have not as yet made a beginning in apple beverage manufacture, (aside from a few brands of mediocre quality high priced apple juice) in spite of the fact that the United States is one of the greatest apple raising countries. This is due principally to three causes: first, but not so very important, being the absence of special cider apple orchards; second, the utilization of only the poorer apples for cider and vinegar manufacture; and third, the utter lack of scientific methods, such as the use of pure yeast cultures, controlled fermentations, etc.

In France in the year 1900 the manufacture of commercial high grade cider exceeded 647,000,000 gallons, while the value of the English output annually (more than 100,000,000 gallons) is estimated at \$15,000,000. Our apple crop is capable of great increase and the manufacture of high grade unfermented and fermented apple juice and cider vinegar might become a great and lucrative industry, particularly when our Federal food and drink laws are enforced to prevent fraud rather than exploit imaginary hygienic controversies.

The chemical composition of the apple, while not so important for our purposes as the composition of the apple juice or must, is of interest, and the average analysis by Browne, who analyzed all the important American varieties, is the most complete yet made (Table 14).

Table 14. Composition of the Apple.

	Percent
Water .....	84.0
Reducing sugars (dextrose and levulose) .....	8.0
Sucrose (ordinary sugar) .....	4.0
Starch (absent in ripe apples) .....	0.1
Cellulose .....	0.9
Lignin .....	0.4
Pentosans .....	0.5
Pectins .....	0.4
Malic acid (free) .....	0.6
Malic acid (combined) .....	0.2
Oil (fatty) .....	0.3
Protein (N $\times$ 6.25) .....	0.1
Ash (Mineral residue) .....	0.3
Undetermined (tannin, etc.) .....	0.2

The ash of the apple is made up principally of potassium carbonate (about 68 percent) and potassium and magnesium phosphates (about

22 percent), the significance of which will become plainer when we consider the total and soluble ash requirements of the apple juice, cider and cider vinegar standards.

It is beyond the scope of this article to go deeply into the chemistry of the various chemical substances found in the apple. Briefly, the reducing sugars are a group of sugars capable of reducing an alkaline copper salt solution to cuprous oxide and they are usually estimated by means of this reaction. The two reducing sugars present in the apple are d-glucose (usually called dextrose),  $C_6H_{12}O_6$ , identical with grape sugar, and levulose, having the same formula and sometimes known as fruit sugar.

The prefix d- refers to the optical effect of a solution of the sugar upon the plane of polarized light and is an abbreviation of *dextro*, meaning that the plane of polarized light is rotated to the right. Levulose, however, is levorotatory (rotating the plane of polarized light to the left) and as the levorotatory effect of levulose is greater than the dextrorotatory effect of the same quantity of d-glucose, the mixture of the two sugars in equal proportions (known as "invert sugar") is levorotatory; and in the apple and apple juice, where levulose predominates, the reading on the polariscope (an instrument for measuring the rotation of the plane of polarized light) is strongly levorotatory, as we will see.

The sucrose in the apple is identical with sugar from sugar cane, sugar beets, etc. Its formula is  $C_{12}H_{22}O_{11}$ ; in solution it is dextrorotatory and, as sucrose, it is not directly fermented by the alcohol forming enzyme (zymase) of yeast, like levulose and d-glucose are. By means of an enzyme in the yeast known as invertase, it is soon converted into invert sugar (equal parts of levulose and d-glucose) and then ferments into alcohol and certain congeneric products.

Starch is a complex carbohydrate related to the sugars, insoluble in water, and having the formula  $(C_6H_{10}O_5)_n$ . It exists in the green apple in considerable quantity (about 4 percent) as microscopic globular granules about 9 microns in diameter, but as the apple ripens it disappears, being in part converted by enzymes in the apple into sugars. The juice from green apples is slimy or turbid (due to suspended starch mainly) and on account of this and the deficiency in sugars, as will be illustrated by analysis later, is not at all adapted for cider or cider vinegar making.

Cellulose has the same general formula as starch but is even more complex, is insoluble even when boiled with dilute acid or alkali, and with lignin and the related pectocelluloses, both of which are sub-



stances closely related to cellulose, constitutes the materials which make up the cell-walls of the apple, the cells being the minute receptacles containing the juice. The analytical item in food analysis known as "crude fiber" is mainly cellulose and the dried marc, or completely leached apple pomace (constituting about 2 percent of the apple) is about one-half cellulose.

Pectins are soluble gum-like substances which under certain influences cause apple juice to gelatinize or "set", thus being of great importance in the manufacture of apple jelly. The principal acid of the apple is malic acid (oxy-succinic acid  $C_2H_3(OH)(COOH)_2$ ), the greater part being in free form, although a certain proportion is in the form of salts known as malates. Separated out and crystallized it forms a white, deliquescent solid substance of intensely acidulous taste. The sourness of a ripe apple is due entirely to its acid content and not to absence of sugars; frequently sour apples are found to contain more sugar than those tasting sweeter. The proportion of free malic acid present may range from 0.1 percent in the "Sweet Bough" to 1.11 percent in the "Red Astrachan" and as high as 2 percent in a very green apple.

The fatty oil of an apple is almost entirely a constituent of the seeds and this is true, to considerable extent, of the nitrogenous matter, which is reported rather vaguely as "protein" or the percent of nitrogen multiplied by 6.25. The "undetermined" matter in the preceding analysis includes, besides tannin, acetaldehyde and the traces of esters from skins, etc., which furnish the apple odor and characteristic flavor. In the apple iso-amyl formate, acetate, caproate and caprylate and geranyl formate and acetate are the principal esters present, but in fermented juice products (cider and vinegar) other esters develop to give the bouquet which has much to do with deciding quality.

Tannin or tannic acid is a rather interesting and important constituent, being the cause of the puckering effect of the crab-apple on mouth membranes, and, what is more interesting, the bitter-sweet taste of the French cider apple. In fact, the expert French cider manufacturer ranks the tannin content of his apple next in importance to the sugar content and insists upon a minimum of 0.3 percent in the apple, and as high as one percent is tolerated. It assists in clarifying the juice products and tends to retard the alcoholic fermentation to the enhancement of the soundness and keeping quality of the cider.

The American and German apples are decidedly deficient in tannin, but the Germans get around the difficulty by using a certain pro-

portion (one part in twenty) of the juice of the Speierling crab-apple (*Pyrus* or *Sorbus domestica*). The use of a similar apple juice rich in tannin or even commercial tannin itself could easily remedy the tannin deficiency in American cider manufacture.

Unless, however, a sufficient percentage of malic acid is present in the fruit and its juice (which is the case in American apples) the oxidation of the tannin by means of a special oxidizing enzyme (oxidase) may cause the juice to turn nearly black, a point which to a moderate degree might be considered advantageous by the cider vinegar manufacturer, who usually wants a rich brown color in his product.

A sweet apple juice with the right proportion of tannin would be a good color producing combination. The rapid browning of apple flesh after the contents of the apple cells become mixed, by cutting or crushing, is due, as stated before, to the oxidation of tannin by the enzyme (oxidase), which is prevented in commercial evaporated apples by exposing to the fumes of burning sulfur (sulfurous acid).

Regarding the variations in the proportion of sugars present in apples, some data are of interest, as on this item the yield of alcohol and, subsequently, acetic acid is directly dependent. The sugars, particularly the sucrose (ordinary sugar), increase as the fruit ripens and decrease slightly as it over-ripens. Reckoning the reducing sugars and the sucrose as "total sugar," the proportion present in various kinds of apples varies considerably. Some of the more famous French cider apples contain as high as 26.3 percent total sugar, the average for the Bramtot being 19 percent and for the Grise-Dieppoise, 20.2 percent! The average for the French cider apples as a whole, however, is between 15 and 16 percent total sugar, which is only 4 percent more than the American apple average, and less than the average for our Golden Russet, which for ten samples was found by Browne to be 16.5 percent. Crab-apples average about 11 percent total sugar.

We will now deal with the composition, etc., of the apple juice and its fermentation into cider, "hard cider" as commonly called in this country. Right here it is interesting to note that a "fruit juice" ("juice of apples" is the wording of the Federal cider vinegar standard, remember) is defined in the proposed supplementary Federal standards as "the clean, unfermented liquid product obtained by the *first pressing* of fresh, ripe fruits." The relation of this requirement to the utilization of "second pressings" in vinegar manufacture, we will endeavor to make plain.

As said in preceding paragraphs, the sugars, particularly the sucrose (ordinary sugar) increase as the apple ripens, the starch of the

green apple being largely if not entirely converted into sucrose. This indicates the desirability of using only fully ripened fruit in the preparation of an apple juice or must, as the juice from unripe fruit is turbid and slimy (from suspended starch) and the alcoholic strength of the cider and subsequent acid strength of the vinegar are proportional to the amount of sugars present.

The sucrose reaches a maximum at just about the same time that the starch in the apple completely disappears, although the proportions of various sugars present continue to change for several months during storage, to the enhancement of the cider and vinegar making value of the apple. The analysis of the ripe apple, in Table 14, shows an average sucrose content of 4 percent. Colby at the California Experiment Station reports as high as 7.8 percent sucrose, his average, however, being but a little over 4 percent.

During storage after ripening, the sucrose, which has attained a maximum coincident with the disappearance of starch, gradually decreases, being converted into reducing sugars (directly fermentable) so that, at a period from one to four months in common storage and as long as from fourteen to seventeen months in cold storage, the sucrose is found to be one percent or less and the reducing sugars about three to four percent higher, except after cold storage when the increase in reducing sugars seems to be somewhat less.

Now as to the proportion of apple juice or must obtainable from apples. The usual French cider industry requirement in this respect is that the apple shall furnish at least 55 percent of its own weight of juice. Any one who has ground up apples in crushing or grating machines and had tried pressing out the juice with the ordinary hand press, knows that only about one-half of the juice in the fruit can be obtained.

It is practically an impossibility to rupture all the cells of the apple by grinding or to extract all of the juice by pressure. With an 80-ton hydraulic press at the Virginia Experiment Station, the best average was 70 percent of the weight of the apple recovered as juice. Moreover, as a considerable percentage of the weight of the recovered juice consists of solids in solution, the actual amount of juice left in the pomace is greater than appears from the percentage of weight recovered.

Eight varieties of summer apples finely chopped and thoroughly pressed in a hand press gave an average of 53.2 percent juice and 43.3 percent pomace, there being an unavoidable loss of 3.5 percent. For eleven autumn varieties the juice recovered was (by weight) 53.9 per-

cent, pomace 44.0 percent, loss 2.1 percent. For nineteen winter varieties the juice recovered was 52.2 percent, pomace 45.6 percent, loss 2.2 percent. Seven varieties of crab-apples gave 57.3 percent juice, 41.4 percent pomace and 1.3 percent loss. Factory machinery will, of course, better these figures, yet it can be readily seen that a considerable proportion of juice and valuable sugar substances may be left in the pomace, and if by saturating with cold or warm water and repressing a diluted so-called "second pressing" can be obtained, fairly rich in fermentable sugars, we see no reason why this should not be allowed to be judiciously used in diluting a rich first pressing juice intended for "vinegar stock." Calculated as the percentage of total sugars of the apple remaining in the pomace, the average value for the above-mentioned summer apples was 47.1 percent; for the autumn apples 44.7 percent; for the winter apples 41.7 percent, and for the crab-apples 38.8 percent. In other words nearly half of the total sugar in the apple is lost unless diluted "second pressings" are utilized.

The Federal standard for cider vinegar, preliminary to fixing a series of analytical limits, defines that vinegar as the "product made by the alcoholic and subsequent acetous fermentation of the juice of apples." In the supplementary food standards, proposed but not yet proclaimed as official, a "fruit juice" is defined as the "clear, unfermented liquid product obtained by the first pressing of fresh, ripe fruit," corresponding in name to the fruit from which it is obtained.

Apple juice, apple must or "sweet cider" is defined and standardized as the "fresh fruit juice obtained from apples, the fruit of *Pyrus malus*, has a specific gravity (20° C.) not less than 1.0415 nor greater than 1.069; and contains in one hundred (100) cubic centimeters (20° C.) not less than six (6) grams and not more than twenty (20) grams of total sugars in terms of reducing sugars, not less than twenty-four (24) centigrams nor more than sixty (60) centigrams of apple ash, which contains not less than fifty (50) percent of potassium carbonate." The term "reducing sugars" was explained in preceding paragraphs and it was also pointed out that the ash of the apple contained on the average about 68 percent of potassium carbonate. This potassium carbonate requires a certain amount of an acid solution of standard strength (tenth-normal acid is usually used) to neutralize its alkalinity, hence the final analytical limit given in the former Federal cider vinegar standard (see Circular 136, Office of Secretary, U. S. Dept. of Agriculture).

From the above facts it would appear that the unlabeled utilization of diluted "second pressings" is ruled out. As concerns apple

juice ("sweet cider") for beverage purposes, the "first pressing" requirement may be desirable and this probably applies to cider (so-called "hard cider"), the alcoholic fermented apple beverage, also. For the manufacture of apple vinegar (so-called "cider vinegar"), particularly for table purposes, where a low acid strength (4 to 4.5 percent) is preferable, provision in the standards should be made for the unlabeled utilization of diluted "second pressings" (defined and standardized if necessary) and the Federal apple vinegar standard modified to accommodate such a practice.

Some analyses of fresh pomace from different groups of apple varieties are shown in the accompanying table (Table 15).

Table 15. Composition of Fresh Apple Pomace

	Moisture	Reducing Sugars	Sucrose (ordinary sugar) (as reducing)	Total Sugars (as reducing)	Tannin	Ash
	Percent					
Summer apples (10 varieties)						
Maximum .....	85.10	6.69	4.78	10.50	0.01	0.44
Minimum .....	80.25	4.33	1.70	7.00	....	0.27
Autumn apples (13 varieties)						
Maximum .....	85.10	6.85	3.85	10.90	0.09	0.61
Minimum .....	70.25	5.54	1.70	7.78	0.01	0.30
Winter apples (19 varieties)						
Maximum .....	84.65	7.09	4.43	11.46	0.17	0.43
Minimum .....	78.65	5.11	1.08	8.09	0.01	0.23
Crab apples (7 varieties)						
Maximum .....	90.00	10.15	4.43	11.76	0.19	0.62
Minimum .....	68.05	5.06	1.30	10.09	0.06	0.31

We have gone into detail somewhat as concerns the composition of apple pomace, because it is upon these data that our contention rests, viz.: that in the manufacture of apple vinegar, at least, the use of a properly standardized diluted "second pressing" should be provided for in the Federal food standards without labeling the vinegar as "diluted." The above data are taken from a bulletin (No. 88) of the Bureau of Chemistry, U. S. Department of Agriculture, which means that at least one member of the Food Standards Commission was aware of the facts of the case. The total sugar (as fermentable reducing sugars) averages as follows for each of the above classes of apples, viz.: summer apples 8.66 percent, autumn apples 9.12 percent, winter apples 9.34 percent, and crab-apples 10.25 percent. Comparing these last figures with the rather liberal average analysis of the whole apple, as given in Table 14, we see an average reduction of but about 2.5 percent in fermentable sugar value.

As to the composition of apple juice or must (see above standard) hundreds of analyses are available and in one hundred analyses, rep-

representing nearly a hundred varieties of American apples (see below) the writer was able to find but one sample (a rich Baldwin juice) that exceeded the specific gravity limit of 1.069 with none below the minimum in gravity and sugar content and ash and only seven samples showing 24 centigrams of ash, which is the minimum called for in the apple juice standard.

The maximum and minimum values obtained in the one hundred analyses of pure apple juice are as shown in Table 16.

Table 16. Composition of Apple Juice.

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	1.042	1.072	1.055
Grams per 100 cc.			
Total solids .....	10.16	18.81	13.61
Reducing sugars .....	4.67	11.63	7.20
Sucrose (ordinary sugar) .....	0.48*	7.05*	3.44*
Total sugars .....	6.74	15.39	10.79
Tannin .....	0.002	0.214	0.06
Ash .....	0.24	0.37	0.30

In addition to these, some data on the acidity (as percent of malic acid) of apple juices are of interest. The range in the above one hundred analyses is from 0.073 percent in the Sweet Bough apple juice to 1.15 percent in the Red Astrachan apple juice. An average would be about 0.55 percent malic acid.

The maximum and average for tannin are both of interest, the latter because it demonstrates the tannin deficiency in American apple juices as compared with the French cider-making requirement of at least 0.2 percent tannin and the former as it shows that certain crab-apples, in this case the Red Siberian crab-apple, are up to or above the French cider-apple juice tannin requirement. As to the exact make-up of the reducing sugars present in apple juice, we have now considerable data.\*

A sample used in some fermentation experiments by Browne showed 7.4 percent levulose to 2.9 percent d-glucose. During the alcoholic fermentation the latter disappeared soon after the sucrose (ordinary sugar) present disappeared, but the levulose persisted in small proportion throughout the alcoholic and acetic fermentations, which explains the slight levorotatory polariscope reading, required in

\* Eoff in the *Journal of Industrial & Engineering Chemistry*, June, 1917, reports on juice from twenty varieties of apples showing the levulose to range from 5 to 8.5 per cent and the d-glucose or dextrose to range from 0.5 to 3.5 per cent. Generally speaking there is usually somewhat over twice as much levulose always present as of dextrose. The sucrose (ordinary sugar) ranged from 0.03 to 3.6 per cent, an average being about 2.5 per cent. Mott in an earlier volume of the same *Journal* (Oct., 1911) reports the ratios between levulose and dextrose in pure cider vinegar, which we will refer to later in this series.

the Federal standard for cider vinegars, and always noticeable in such if care be exercised in the test. Certain cider bacteria select levulose and destroy it, others select d-glucose (dextrose). In fresh apple juice Browne reports for eleven varieties of summer and winter apples a range of from  $-9.6^{\circ}$  to  $-24.5^{\circ}$  Ventzke, using a 200 millimeter tube, the average being about  $-18.0^{\circ}$ ; a fairly high levorotatory reading.

The analysis of a particularly rich juice from a green Baldwin apple (Table 17) is of interest. Only very rarely would the juice from a green apple approximate these figures, which shows, aside from the undesirable turbidity, etc., the unfitness of unripe apples for cider vinegar making.

Table 17. Analysis of a green Baldwin apple juice.

Appearance .....	Slimy and turbid
Starch (in the apple) .....	5.14
Specific gravity .....	1.0474
Total solids (in the juice) .....	11.36
Reducing sugars .....	6.64
Sucrose (ordinary sugar) .....	1.56
Total sugars (after inversion) .....	8.28
Malic acid .....	1.18
Alcohol yield (sugars x 0.46) .....	3.81
Acetic acid yield (alcohol x 1.20) .....	4.57

The above alcohol and acetic acid yields are less than theoretical, but in actual practice the vinegar obtained from even such a rich juice as the above would in all probability be below standard.

As concerns the analytical values on "second pressings" the writer has been able to find but one analysis (by Browne). Much depends, of course, upon how much water is used for wetting the pomace and how thoroughly the same is macerated with the water before re-pressing.

Table 18. Analysis of "Second Pressing."

Specific gravity .....	1.0376
	Percent
Total solids .....	9.14
Reducing sugars .....	6.87
Sucrose (ordinary sugar) .....	1.49
Ash (mineral residue) .....	0.20

Such a juice as shown in Table 18 would furnish a 4 percent, possibly a 4.5 percent acetic acid vinegar, but in total solids and ash the vinegar would, of course, be below standard. However, people buy apple or cider vinegar for the acid taste and apple flavor and bouquet and not for the two or three percent of mineral matter, gums, etc., that may be incidentally present. The utilization of diluted "second pressings" (standardized preferably) should by all means be allowed in

conjunction with straight apple juice in vinegar manufacture. Much of the diluted "second pressing" juice is now used in making cider jelly or so-called "boiled cider," which in turn has been extensively used to fraudulently sophisticate true apple vinegar.

Diluted spirit vinegar, reinforced with this jelly and possibly mixed with some true vinegar to furnish flavor, was for a long time considered a very shrewd adulteration. Even yet the very liberal reducing sugar limit in the original apple vinegar standard renders the practice fairly safe if judiciously regulated. An analysis of cider jelly, by Browne, is shown in Table 19.

Table 19. Analysis of a Cider Jelly

	Percent
Moisture .....	44.54
Reducing sugars .....	49.50
Sucrose (ordinary sugar) .....	2.18
Malic acid .....	3.61
Pectin .....	1.60
Ash (mineral residue) .....	1.39

The manufacture of cider as a beverage of quality is considered by experts to be more difficult and to necessitate more careful control than the manufacture of most grades of wine. Only a very small proportion of what is sold as "cider" in this country has a claim to the name and a still smaller proportion, in fact what might be called a negligible quantity only, can be considered as a beverage of quality.

In England and continental Europe, and in France particularly, the manufacture of high grade ciders constitutes an important industry, rivaling the wine industry. In 1898 over one million citizens of France were entered upon Government reports as cider manufacturers and from the apple crop of 1900 more than 647,000,000 gallons of commercial good quality cider was produced, not taking into account that produced for home consumption.

We are not going so far as to say that the manufacture of a high grade cider is a prerequisite to the production of good apple vinegar. Compared with much of the dilute acid sold for condimental purposes in this country, a very poor apple vinegar is a superior article and commands a higher price. Yet it has been a matter of frequent mention in technical literature that the bulk of the apple vinegar sold in this country was just about on a par in quality with the cider made. The causes, such as the utilization of rotten, unripe and generally inferior fruit and careless, unscientific, and slovenly methods of manufacture, have been dwelt upon in said literature so often that to repeat them here is impracticable.



A high grade cider may not be a prerequisite to the production of a fairly good grade vinegar, but as the acetic fermentation, as now conducted in rapidly acting generators, involves little more than the conversion of alcohol into acid, it will be admitted that the better the alcoholic fermented product (cider or "vinegar stock") the better the condimental product (vinegar) will be. The vinegar obtained by the old fashioned cask method of fermentation was a superior product as regards flavor and bouquet, and to counteract the inferiority of the commercially necessary generator process, we must look more to the nature and quality of the apple juice, both fresh and alcoholically fermented. A cider, carefully made with well developed flavor and bouquet and passed through a clean, well controlled generator, may yield even a better product than the vinegar often made by the cask fermentation.

It is impracticable to go into the manufacturing details of cider production here, as the technique and related details of the various methods of procedure in different countries would fill a good sized volume. To the would-be progressive cider and apple vinegar manufacturer, however, the author can recommend several Government bulletins to be had for the asking or, at the most, a nominal fee of a few cents, which portray in a truly fascinating way what has been accomplished in France, Germany and England in the manufacture of cider, the methods in vogue (complete details) in each country and the results of experimental work in this country on scientifically controlled fermentation, utilizing the characteristically inferior apple juices available, or rather, allotted to cider and vinegar manufacture in America.

These are Bulletins 71 and 88 of the Bureau of Chemistry, U. S. Dept. of Agriculture, entitled "A Study of Cider Making in France, Germany and England," and "The Composition of Cider as Determined by Dominant Fermentation with Pure Yeasts." The sole author of the first and the principal author of the second is Dr. William B. Alwood of Charlottesville, Va., Enological Chemist of the Bureau of Chemistry.

The first or alcoholic fermentation of apple juice is due, as is well known, to the activities of the yeast cell, and to quote Bulletin 71, "the quality of the resultant product depends upon whether desirable or undesirable organisms gain the mastery in the must (or juice) during initial fermentation. In order to insure the ascendancy of the true yeasts in the early stages, and thus give them the control of the entire process of fermentation, there has recently been developed the practice

of sowing the must with pure cultures of yeast. Very often special races of yeasts are used to secure certain desired qualities of bouquet, etc., in the finished product. In Germany practically all the important factories employ these pure cultures." Various fungi will convert sugar into alcohol, but the yeasts *Saccharomyces cerevisiae* are the true alcoholic fermentation organisms. False yeasts, such as the *Apiculatus* and other "wild" forms, are frequently the cause of undesirable fermentation results. In practical factory work it has not been found advisable to sterilize or even pasteurize the juice, as the finer natural flavors, due to esters, etc., in the juice, are injured by attempts at sterilization.\* If one sows a sufficient amount of a fresh culture of a strong yeast into the freshly expressed juice, a controlling or dominant fermentation is easily secured and the time of the alcoholic fermentation reduced one-half.

The French method of racking off after the quieting down of the first or violent fermentation is preferred by Alwood to the German method of completely fermenting out the sugars before racking off. The latter method gives a better standardized product, but one lacking in the quality of the French products. The preferable temperature of the yeast fermentation is between 55° and 65° F., but is more rapid when between 65° and 75° F.

The direct agents in the process are two enzymes produced by the growing yeast plants and known as invertase and zymase. The former converts any sucrose (sugar) into alcoholic fermentable sugars (invert sugar or reducing sugars) while the zymase is the alcohol and carbonic acid-forming enzyme. Various secondary reactions also occur whereby small quantities of glycerin, succinic acid and certain aromatic products of flavoring value are formed. About one one-hundredth of the total amount of fermentable sugars present is utilized by the yeast cells for building up cell tissue. Certain nitrogenous substances in the juice are also important as nutriment for the yeast plant. In the German fermentation industries, preparations of zymase are being used in place of yeast cultures.

The theoretical reaction of alcoholic fermentation is chemically expressed as follows:—



\* In the *Journal of Industrial and Engineering Chemistry* for April, 1925, the enological experts of the California State Experiment Station report very favorably on the use of sulfurous acid in the manufacture of fermented apple juices, showing that there are a more complete fermentation of the sugars, an increased yield of alcohol, a better flavor, more rapid clearing, freedom from lactic bacteria and later, in the acetic fermentation, a more rapid change of alcohol to acetic acid. The original article should be consulted for methods, etc.

or one molecule of reducing sugar yields two molecules of alcohol and two molecules of carbonic acid (carbon dioxide). According to this 100 parts of the sugar should yield 51.11 parts of alcohol, 48.89 parts of carbon dioxide being given off. As said above, however, some of the sugar is utilized as food by the yeast and according to Pasteur from 100 parts of reducing sugar can be obtained but 48.5 parts of alcohol and 46.6 parts carbon dioxide, about 3.3 parts of glycerin and 0.6 parts of succinic acid also being formed.\* Kulisch reports from 0.38 gram to 0.59 gram per 100 cc. of glycerin in ciders, the ratio of glycerin to alcohol being approximately 1 to 10.

In actual practice the proportion of alcohol obtained is about 46 parts (by weight) from 100 parts (by weight) of fermentable reducing sugar. During the alcoholic fermentation of apple juice into cider, the acetic fermentation, due to certain bacteria acting on the alcohol, usually gets slightly started. More than 0.5 percent of acetic acid will retard the alcoholic fermentation considerably and Lafar has shown that out of 15 different varieties of yeast, only three were able to cause fermentation, when the acetic acid exceeded 1 percent. This shows the folly of attempting to hasten the manufacture of vinegar by mixing fresh apple juice with vinegar, a practice not unheard of.

The slight proportion of acetic acid formed during the alcoholic fermentation of apple juice probably accounts for the small amount of the reducing sugar, levulose, which escapes conversion into alcohol and, remaining in the finished product, gives the characteristic levorotatory polariscopic reading. The following synopsis of the alcoholic fermentation of apple juice as determined by Browne shows the acetic acid to have reached the alcoholic fermentation restraining limit before all the levulose had fermented.

As said previously, the sucrose (ordinary sugar) is first to disappear. The d-glucose ("grape" sugar or dextrose) soon follows suit, but, as described above, the levulose persists in small proportion to the end of the acetic fermentation. The pectin of the apple juice disappears almost completely during the above outlined fermentation, due possibly to sedimentation. During the last half of the process, the esters (formerly called ethers) begin to manifest themselves and in the above instance at the time of the highest alcoholic content, the "ester number" was equivalent to practically 0.1 percent ethyl acetate.

One of the most interesting series of changes is that of the malic acid, the characteristic natural acid of the apple. At the end of the

\* The complete chemical reaction of alcoholic fermentation is quite complex. References can be found in *Chemical Abstracts*, Aug. 20, 1913, p. 2768,

Table 20. Alcoholic Fermentation of Apple Juice.

Date	Specific Gravity	Total Solids	Sucrose	D-glucose (Dextrose)	Levulose	Total Sugar
				Percent		
Nov. 16.....	1.0577	13.75	2.93	2.90	7.38	13.36
Nov. 30.....	1.0462	12.25	1.20	2.86	7.29	11.43
Dec. 16.....	1.0331	9.48	0.50	2.06	6.28	8.87
Jan. 5.....	1.0133	5.92	0.09	1.21	2.88	4.19
Jan. 19.....	1.0067	4.53	0.01	0.44	2.02	2.47
Feb. 16.....	1.0013	2.89	0.00	0.21	1.17	1.38
Mar. 9.....	0.9982	2.24	0.00	0.07	0.54	0.61
Apr. 3.....	0.9968	2.10	0.00	0.00	0.30	0.30
May 4.....	0.9969	1.94	0.00	0.00	0.24	0.24
July 27.....	0.9959	1.80	0.00	0.00	0.11	0.11

	Alcohol	Acetic Acid	Malic Acid	Ash	Levorotation (400 mm. tube)
					Percent
Nov. 16.....	0.43	0.04	0.43	0.26	—44.18° V.
Nov. 30.....	1.67	0.05	0.43	0.24	—53.78
Dec. 16.....	3.05	0.06	0.43	0.24	—50.45
Jan. 5.....	5.32	0.08	0.40	0.24	—29.60
Jan. 19.....	6.03	0.09	0.38	0.24	—18.80
Feb. 16.....	6.70	0.11	0.30	0.25	—11.60
Mar. 9.....	6.92	0.11	0.23	0.25	— 5.30
Apr. 3.....	6.93	0.17	0.21	0.25	— 3.40
May 4.....	7.00	0.27	0.21	0.26	— 2.30
July 27.....	6.86	0.52	0.20	0.26	— 1.50

above alcoholic fermentation it had *decreased* more than 50 percent. During the acetic fermentation it practically disappears, a properly fermented and aged cider vinegar containing none, a fact contrary to the general idea prevalent among cider vinegar manufacturers.

This phenomenon is due to the activity of certain bacteria, especially *Micrococcus malolacticus*, which convert malic acid into lactic acid and certain volatile acids. Sterilization prevents this and a low fermentation temperature tends to retard it. The well known test with lead acetate solution, given by genuine cider vinegars and thought to be due to malic acid, is really due to other extractive matters of the apple.

The proposed Federal standard for alcoholic fermented apple juice, or cider, defined it as "the product made by the normal alcoholic fermentation of apple juice and the usual cellar treatment, and contains not more than seven (7) percent by volume of alcohol and in one hundred (100) cubic centimeters (20° C.), of the cider, not less than two (2) grams nor more than twelve (12) grams of solids, not more than eight (8) grams of sugars, in terms of reducing sugars, and not less than twenty (20) nor more than forty (40) centigrams of cider ash."

This standard is absurd for "dry" ciders in several particulars, as will be evident from the subjoined analytical data representing maximum and minimum values reported in the Bureau of Chemistry bulletins on cider of known normality and purity. The maximum limits for total solids and sugars tolerates the addition of much sugar for fraudulent purposes while the minimum limit for total solids would rule out many high grade ciders of known purity. The data in Table 21 represent about 125 pure ciders.

Table 21. Composition of Ciders (Apple Wines).

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	0.9959	1.0398	1.0086
Alcohol (percent by volume) .....	1.60*	7.83	5.19
Grams per 100 cc.			
Total solids .....	1.48	10.81*	3.72
Sugar (as reducing) .....	0.02	7.46*	1.69
Acetic acid .....	0.01	1.96	0.23
Malic acid .....	0.13	0.55	0.29
Ash (mineral residue) .....	0.18	0.39	0.27
Levorotation (400 m.m. tube) .....	-0.18° V.	-5.28° V.	-2.34° V.

\* Characteristic of so-called "small ciders," i.e., underfermented.

The averages for total solids and sugars are rather high, for fully fermented ciders particularly, due to the inclusion of data on underfermented products. If the term cider is to be interpreted as "dry" cider ("hard cider") and by "normal fermentation" is understood a complete fermentation, it would appear that the proposed Federal standard for cider needs considerable revision. For conversion into cider vinegar, a completely fermented product is desirable of course. Ciders from fermented pomace vary from a normal cider considerably, being high in pentosans, resulting from the fermentation of the apple cell-wall material, especially. An analysis by the U. S. Bureau of Chemistry showed alcohol 3.32 percent, total solids 6.44 percent, non-sugar solids 4.5 percent, of which 0.8 percent was pentosans, 0.5 percent was lactic acid and the balance was ash, galactans, etc.

By a "normal alcoholic fermentation" should be understood a complete fermentation of the juice into a so-called "dry" product containing the minimum of unfermented sugars. In various ways, however, such a complete fermentation is purposely or unintentionally prevented and the proposed Federal standard for cider is so set, as pointed out previously, as to accommodate a so-called "small" or underfermented cider containing relatively little alcohol and a larger percentage of sugars. Thus a contradiction exists in the standard for cider, which however is not taken into consideration in the standard

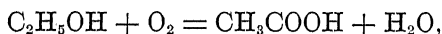
for cider vinegar. *In other words, the analytical limits in the cider standard allow a product which when made into vinegar would be illegal according to the cider vinegar standard.*

The fermentation of cider into vinegar consists of little more than a transformation of the alcohol into acetic acid under the influence of certain bacteria, notably *Mycoderma aceti* and *Bacterium Pasteurianum*. These bacteria require plenty of oxygen (air) and the fermentation proceeds best at a temperature of 65° to 75° F. The acetic bacteria possess the peculiarity of forming a gelatinous enveloping membrane which coalescing forms a jelly-like film, known as "mother vinegar," containing the bacteria imbedded therein. The *Bacterium xylinum* forms, by action on levulose, a particularly thick, cellulose-containing "mother" and appears to be concerned in the degenerative fermentation of vinegar, by which the acetic acid is destroyed and the resulting product even rendered alkaline in reaction. Certain acetic bacteria form lactic acid when alcohol is present. The same bacteria also attack malic acid.

The reader is assumed to be familiar with the details and manipulation of the cask and "generator" methods of fermenting cider or "vinegar stock" into vinegar. The "generator" process requires but a very small fraction of the time required for a "cask" fermentation and for factory purposes is the only practicable method, of course.

A superior product is claimed to be obtainable by the "cask" method, supposedly due to the aromatic by-products which are formed during the year or so required to complete a fermentation of cider into vinegar when left to ferment spontaneously in a cask or barrel. We are inclined to believe however that much of the "bouquet" is a result of the alcoholic fermentation and if the latter has been conducted properly a superior product is obtainable by a carefully regulated "generator" process.

The chemical equation expressing the fermentation of alcohol into acetic acid is as follows:



or one molecule of alcohol plus one molecule of oxygen yields one molecule of acetic acid ( $\text{CH}_3\text{COOH}$ ) and one molecule of water. Acetaldehyde and acetal are formed as intermediate products. From 100 parts (by weight) of alcohol should be obtained theoretically 130.4 parts of acetic acid. In actual practice this yield is seldom if ever reached, even when the alcohol lost by evaporation in an overheated generator is allowed for. On an average 100 parts (by weight) of alcohol will

furnish about 120 parts of acetic acid. Acetic acid poisons mucous membranes when above 12 percent strength.

The Federal standard for apple or "cider" vinegar calls for at least 4 percent of acetic acid. A frequent State requirement, and the customary and preferable strength for table purposes is 4.5 percent acetic acid. To obtain this strength, it is but necessary, according to the above, that the cider contain from 3.8 to 4 percent (by weight) of alcohol; and by reference to the synopsis of alcoholic fermentation, given previously, it will be seen that if a cider of that strength was submitted to acetic fermentation, a large percentage of reducing sugar and a high ratio of reducing sugar to total solids would be found in the vinegar, which, according to the original Federal standard, would condemn it (unjustly) as illegal.

Most vinegar manufacturers allow the formation of as much alcohol as possible in the cider or "vinegar stock," of course, and the vinegar obtained by careful acetic fermentation of such will average about 6 percent acetic acid. To reduce this, by watering, to the desired 4.0 to 4.5 percent acid strength is not only an illegal procedure, unless stated on the label, but may possibly bring the total solids, etc., below the legal minimum, especially in those states which have not yet discovered that a requirement of 2 percent total solids, in properly fermented cider vinegar, is a scientific absurdity. The alternative is to stop the alcoholic fermentation as outlined above and then be accused of having added unfermented apple material (boiled cider or apple jelly) to the product. Most manufacturers aim to get a maximum acetic acid yield, then dilute with water and label as diluted. If thus labeled, the Federal food inspection chemists ignore the standard for total solids.

Another way in which an apple vinegar may be found to have a high reducing sugar value and ratio (to total solids), without the accusation of added jelly or boiled cider being true, is as a result of the acetic fermentation getting started before the alcoholic fermentation has finished, whereby the latter is stopped, with the result that a high percentage of reducing sugars is found in the vinegar. The not infrequent practice of adding fresh apple juice to fermenting vinegar, with the false hope of hastening its fermentation into cider and later, vinegar, is also a cause of a high reducing sugar value. Yet another, recently coming to the writer's attention in connection with a contemplated Federal prosecution, is the presence of a preservative in an apple juice, which later it may be found necessary to convert into

vinegar, with the result that the complete fermentation of sugars into alcohol is prevented.

In Table 22 is given a continuation of Browne's synopsis of the alcoholic and acetic fermentation of an apple juice containing originally 13.36 percent total sugars.

Table 22. Acetic Fermentation.

Date		Specific Gravity	Total Solids		Total Sugar	Percent				Levorotation (400 mm. Tube)
			Levulose			Alcohol	Acetic Acid	Malic Acid	Ash	
July 27.....	0.9959	1.80	0.11	0.11	6.86	0.52	0.20	0.26	—1.50° V.	
Aug. 14.....	0.9965	1.53	0.11	0.11	6.66	1.11	0.17	0.26		
Oct. 2.....	0.9988	1.48	...	...	6.01	1.77	0.16	0.26	—1.20	
Nov. 27.....	1.0017	1.42	...	...	4.80	2.59	0.15	0.26		
Feb. 14.....	1.0037	1.40	...	...	4.54	3.67	0.14	0.26	—1.20	
Apr. 20.....	1.0060	1.37	0.18	0.18	3.77	4.31	0.14	0.26		
July 31.....	1.0113	1.70	0.22	0.22	2.61	5.98	0.11	0.25	—1.20	
Final .....	1.0140	1.80	0.26	0.26	0.00	9.00	0.07	0.25		

Somewhat more than a year later, after a degenerative fermentation had set in, the acidity had decreased to 3.33 percent, the total solids had increased to 2.4 percent (due more or less to concentration in volume of vinegar) and the reducing sugar had increased to 1.2 percent. The acetic bacteria themselves consume the acetic acid forming carbon dioxide and water, according to Pasteur, and the *Bacterium xylinum*, according to Bertrand, can convert the glycerin present into dioxycetone, which reduces a copper solution and would be reckoned as reducing sugar unless corrected for in analysis.

Certain molds, even when dead, have the property of destroying acetic acid in vinegars and there are several ways that the glycerin normally present in cider and cider vinegar can be partially lost, other than by being converted into dioxycetone as mentioned above. Thus, in addition to the possibility of glycerin being oxidized to glyceric aldehyde, in generators where oxidizing conditions become too active, as pointed out by Ross, we know that certain fungi convert glycerin to citric acid; that *Bacterium aceti* and other acetic bacteria oxidize it to simpler compounds such as carbon dioxide and water; and in bitter wines and ciders, the glycerin has been found to be converted into acrolein by certain bacteria.

As said previously, the malic acid of apple juice and cider can be lost entirely, in a fully fermented vinegar, due to action of *Micrococcus malolacticus*, which converts malic acid to lactic acid. Acetic bacteria may also decompose malic acid into simpler compounds. Lactic acid is the chief non-volatile acid of cider vinegar.



If any dextrose (d-glucose) is present in the "vinegar stock" undergoing slow fermentation, it can be converted into gluconic acid by *Bacterium aceti*, according to Brown and Boutroux; and traces of formic acid can also be formed during the acetic fermentation, from the acetylmethylcarbinol always present. The maximum so far reported for this natural formic acid is 0.009 percent and the presence of a greater proportion has been considered as proof of the addition of commercial acetic acid, which always contains more or less formic acid.

The acetylmethylcarbinol mentioned above is the chief constituent of the analytical item "volatile reducing substances" and is always formed in appreciable quantities (0.14 to 0.34 percent) during the acetic fermentation of apple, wine and probably other fruit juice vinegars. It reduces an alkaline copper salt solution, similar to reducing sugars, and is usually reported in terms of "invert sugar."

As to the make-up of the sugars, always present in cider vinegar in small proportion, there seem to be some contradictions in the literature on the subject. In the above synopsis of acetic fermentation, as reported by Browne, the dextrose (or d-glucose) had completely disappeared by the time the acetic fermentation got started. Possibly this was due to the slowness of the cask fermentation employed in the experiment. Quicker methods using "generators," etc., seem to leave traces of dextrose, but there is, on the average, five times as much levulose present in cider vinegar as there is dextrose (see 1912 Report of the Mass. State Board of Health and *Journal of Industrial and Engineering Chemistry* for October, 1911). When the dextrose begins to equal the levulose, and especially if it exceeds the levulose, there is good reason to suspect the presence of unfermented apple material, such as apple jelly or boiled cider.

The proportion of non-sugar solids is a somewhat important item in modern vinegar chemistry, the Federal food inspection chemists claiming that the proportion present in a pure undiluted cider vinegar should never be less than 1.25 percent. It is, without doubt, a more reliable item than the percent of total solids, on account of the various ways in which the sugars in vinegar may be unusually high (see above), but there are considerable data on samples of known purity to show that cider vinegars may show considerably less than 1.25 percent. Thus Hartman and Tolman, while in the Federal food inspection service, showed that in vinegars made from cider which had been stored for about one year there was a loss of approximately 50 percent of the non-sugar solids, due to precipitation of gums, pectin, etc.; one un-

diluted vinegar ultimately showing but 1.2 percent total solids and 1.1 percent non-sugar solids. In some cask fermentation vinegars made at the New York State Experiment Station, the non-sugar solids showed less than 1 percent, but in general it may be said that the non-sugar solids in the average cider vinegar will range from 1.2 to 2.9 percent, averaging about 1.9 percent.

The ratio of the total ash of cider vinegar to the non-sugar solids is also of some legal analytical value, and will generally range from 12 to 27 percent with an average of 19 percent. However, a low non-sugar content with a normal ash content will figure out as high as 30 or 31 percent, as in the stored cider vinegars mentioned above. The normal ratio of the sugars to the total solids of cider vinegar, is about 20 percent, but the range depends upon many factors and may be above the over-liberal 50 percent allowed in the former cider vinegar standard and may be as low as 6 percent in a vinegar made from a very "dry" cider. The more commercially efficiently the alcoholic fermentation is conducted, the less sugar there will be in a cider vinegar and the lower the ratio of sugar to total solids will be.

As to the "bouquet"-producing substances in cider vinegar, we have not many data. Hartman and Tolman found from 0.8 to 0.9 percent of esters (as ethyl acetate) and in well aged fruit vinegars, the odor of ethyl acetate is often very strong. Probably some of the original esters of the apple, referred to previously, are also present in the finished vinegar.

The pentosans have been previously referred to, and are always found in small proportion in cider vinegars. In vinegars made from the juice of fermented pomace or adulterated with a jelly made from fermented pomace pressings, the pentosans will show high, due to the fermentation of the apple cell-wall material into pentosans. Over 0.25 percent pentosans in cider vinegar is suspicious.

There is usually a little alcohol left unfermented in cider vinegar, ranging from 0.03 to as high as 2 percent (by volume) in a carelessly handled product. In ageing, it is desirable to have a little alcohol present to assist in the formation of esters for improving "bouquet."

The former Federal standard for apple or cider vinegar defined it as "the product made by the alcoholic and subsequent acetous fermentations of the juice of apples, (which) is levorotatory, and contains not less than four (4) grams of acetic acid, not less than one and six-tenths (1.6) grams of apple solids, of which not more than fifty percent (50 percent) are reducing sugars, and not less than twenty-five hundredths (0.25) gram of apple ash in one hundred (100) cubic

centimeters (20° C.); and the water-soluble ash from one hundred (100) cubic centimeters (20° C.) of the vinegar contains not less than ten (10) milligrams of phosphoric acid ( $P_2O_5$ ), and requires not less than thirty (30) cubic centimeters of deci-normal acid to neutralize its alkalinity."

In Food Inspection Decision 193, issued Sept. 15, 1924, this standard was simplified by eliminating all analytical limits except the requirement of not less than four (4) grams of acetic acid. To the official chemist is left the question of deciding if the definition part of the standard has been complied with, from a study of such data as we have described.

For practical purposes "grams per 100 cubic centimeters" may be read as percent in vinegars, where the specific gravity is so near that of water.

The alkalinity of the water-soluble ash is due, as we have intimated previously, to the fact that the ash of the apple (and derived products) contains a large proportion (60 to 70 percent) of potassium carbonate; and the above requirement for phosphoric acid in the water-soluble ash is based upon the fact that potassium and magnesium phosphates make up from 20 to 25 percent of the ash.

The levorotatory reading in a polariscope, we have already pointed out, is due to traces of the reducing sugar, levulose, remaining in the finished vinegar. In a pure product, "apple solids" and "apple ash" are synonymous with "total solids" and "total ash."

Table 23 represents about 100 analyses of pure cask-fermentation and generator-made cider vinegars, before being reduced with water.

Table 23. Cider Vinegar Analyses.

	Minimum	Maximum	Average
Specific gravity (15.6° C.) .....	1.0126	1.0275	1.0177
Grams per 100 cc.			
Acidity (as acetic acid) .....	3.24	9.96	5.21
Non-volatile acid (as lactic) .....	0.05	0.30	0.18
Alcohol (by volume) .....	0.03	2.00	0.35
Glycerin .....	0.23	0.46	0.30
Total solids .....	1.20	4.45	2.40
Reducing sugars (as invert sugar) .....	0.11	1.12	0.47
Volatile reducing substances (as invert sugar)....	0.14	0.34	0.20
Non-sugar solids .....	1.00	2.90	1.90
Pentosans .....	0.08	0.22	0.16
Formic acid .....	0.0003	0.009	0.003
Volatile esters (as ethyl acetate) .....	0.30	0.91	...
Total ash .....	0.20	0.57	0.38
Soluble ash .....	0.17	0.51	0.34
Phosphoric acid in soluble ash .....	0.007	0.040	0.017
Phosphoric acid in insoluble ash .....	0.004	0.032	0.012
N/10 acid to neutralize soluble ash .....	21.5cc.	56.0cc.	35.0cc.
Levorotation (200 m.m. tube) .....	-0.2° V.	-3.6° V.	-1.4° V.
Sugars in total solids .....	5.3%	43.3%	20.2%
Total ash in non-sugar solids .....	12.0%	30.0%	19.0%

A glance at the above column of minimum values will show almost every item of the analytical limits of the former cider vinegar standard to have been transgressed by cider vinegars of known purity. Only the property of levorotation and the very high 50 percent ratio allowed for "sugars in total solids" are not violated. In connection with the minimum for glycerin (reported by Hartman and Tolman), there is good reason to believe that under certain somewhat abnormal conditions, a considerably lower figure may naturally result. The minimum acidity reported above is obviously abnormal and it may have been a deteriorated vinegar or an underfermented one.

Browne gives an analysis of an underfermented cider vinegar (Table 24).

Table 24. Analysis of an Underfermented Cider Vinegar.

Specific gravity .....	1.005
	Percent
Acidity (as acetic acid) .....	2.60
Alcohol (by weight) .....	2.21
Total solids .....	1.36
Reducing sugars .....	0.16
Total ash .....	0.28

Such a vinegar, if the acetic fermentation were allowed to be completed, would be found to be up to standard.

The methods of adulterating apple or cider vinegar are numerous. One of the commonest ways is the substitution of vinegar made by fermenting a water extract of dried apple products, such as dried "chops" and dried "cores and skins," both by-products from the evaporated apple industry. If carefully made, the resulting vinegar (which, to be correctly labeled, should be called "dried apple vinegar") will, of course, analyze much the same as a fresh juice apple or cider vinegar, and in itself constitutes often a very good vinegar, even though the natural ethereal flavoring matters of the apple have been lost by drying. It was usually detectable by testing for the sulfur, introduced during the drying of the apple by-products. When factory chemists devised the scheme of removing the sulfur-acid salts with barium compounds (poisonous), the spectroscopic test for traces of barium was devised by the official chemists.

The older methods of adulteration were usually crude, consisting of mixing apple jelly and other solid yielding material with commercial acetic acid or spirit vinegar. Then as the Federal standard began to be enforced, factory chemists would add mineral salts to furnish "ash" and "alkalinity" and "phosphoric acid in the soluble ash"

and even the careful addition of glycerin has been practised since the inspection chemists have been testing for that.

The Federal standard will detect the clumsy adulterations of early days, but is practically worthless for detecting the scientifically guided adulterations of later times. Only a more or less complete analysis, similar to the above, will show all possible forms of adulteration; although, if one has reason to suspect a certain form of adulteration, oftentimes one or two specific analytical items will suffice to reveal that special form of adulteration. The present-day legal chemistry and legal control of apple or cider vinegar is a very advanced subject, requiring much experience and knowledge of data and its interpretation.

### WINE VINEGAR

As pointed out in our introductory note, certain vinegars are so extensively used, or were so exclusively used originally, in certain countries, as to have become what may be called the "national vinegar" of that country. In fact, in food inspection circles it is customary to restrict the use of the single term vinegar to that particular national product; thus vinegar in America means cider vinegar only, and in France and Italy wine vinegar is the national vinegar.

Just as wine itself is the oldest fermented beverage, so is wine vinegar the oldest type of vinegar. To go into the many details of manufacture involved in the production of the many varieties of wine from grape juice is beyond the scope of this article. The analytical data shown in Table 25 on the juice of the grape are according to König and others. See also Table 3A.

Table 25. Analyses of Grape Juice.

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	1.069	1.2075	1.1024
		Percent	
Total solids .....	17.90	48.47	25.51
Sugars (reducing sugars) .....	12.89	35.45	19.71
Acidity (as tartaric acid) .....	0.20	1.18	0.64
Ash (mineral residue) .....	0.20	0.63	0.40
Polarization (200 mm. tube) .....			-5.5° V.

Just as the poorer grades of apples are used for apple vinegar making in America, so are the poorer grades of grape juice and wine used for wine vinegar making abroad.

Disregarding the effervescent wines (champagne) and the various wines which have been "fortified" with brandy or alcohol (port, Madeira and sherry) and in which acetic fermentation is impossible,

except after dilution, we may consider the following minimum and maximum analytical figures for wines:

Table 26. Simple Grape Wines (700 analyses).

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	0.990	1.023	0.998
		Percent	
Alcohol (by weight) .....	4.00	12.78	8.93
Alcohol (by volume) .....	5.00	15.79	11.09
Solids ("extract") .....	1.09	9.69	3.25
Sugars (reducing sugars) .....	0.03	6.55	0.73
Glycerin .....	0.46	1.09	0.59
Acidity (as tartaric acid) .....	0.49	1.14	0.68
Ash (mineral residue) .....	0.11	0.74	0.28
Potash ( $K_2O$ ) .....	0.07	0.30	0.09
Phosphoric acid ( $P_2O_5$ ) .....	0.02	0.05	0.03
Tannin and color .....	0.02	0.36	0.21*
Polarization (200 mm. tube) .....	+0.6° V.	-18.6° V.	-1.50° V.

\* 0.04 for white wines.

The given maximum value for sugar represents a decidedly under-fermented (sweet) wine rather than a sugared (chaptalized) product. Chaptalizing, or the addition of sugar to the original grape juice (must) for the purpose of increasing the alcohol content, should not, by the way, be confused with the fraudulent practice so common in some countries, known as "gallizing," or diluting the original juice with a thin sugar syrup.

The Federal standard for grape wine is as follows:

"Wine is the product made by the normal alcoholic fermentation of the juice of sound, ripe grapes and the usual cellar treatment, and contains not less than seven (7) nor more than sixteen (16) per cent of alcohol, by volume, and in one hundred (100) cubic centimeters (20° C.) not more than one-tenth (0.1) gram of sodium chloride, nor more than two-tenths (0.2) gram of potassium sulfate, and for red wine not more than fourteen-hundredths (0.14) gram and for white not more than twelve-hundredths (0.12) gram of volatile acids produced by fermentation and calculated as acetic acid. Dry wine is wine in which the fermentation of the sugars is practically complete and should contain less than one gram (per 100 cubic centimeters) of sugar, and for red wine not less than 1.6 grams and for white wine not less than 1.4 grams of sugar-free grape solids. Sweet wine is wine in which the alcoholic fermentation has been arrested, and contains not less than 1 gram of sugar per 100 cubic centimeters. The ash requirements for red wines is at least 0.16 gram (per 100 cc.), and for white at least 0.13 gram." The proposed standard for grape juice is given in Chapter I.

In the data for grape juices given above König reports a product which, on the basis of grams per 100 cc., contained 42.5 grams of reducing sugars. This may have been a partially concentrated juice,\* and the proposed limit of 28 grams per 100 cc. for reducing sugars is probably high enough. The standards for red and white wines, however, do not accommodate a number of high-grade white wines of known purity in which the ash has been found below the legal limit of 0.13 gram per 100 cc. and both red and white wines in which the alcohol was considerably less than 7 percent (by volume). Some of the white wines below standard in ash took prizes at the Paris Exposition (see Bull. 72, Bureau of Chemistry, U. S. Department of Agriculture), and a number of these, together with some of the red wines, also contained considerably more than the legal amounts of volatile acids.

In both wine and vinegar, particularly the former, grams per 100 cubic centimeters may be read as percent (by weight) for practical purposes. The former Federal standard for wine or grape vinegar defines it as "the product made by the alcoholic and subsequent acetous fermentations of the juice of grapes, and contains in one hundred (100) cubic centimeters not less than four (4) grams of acetic acid, not less than one (1) gram of grape solids and not less than thirteen-hundredths (0.13) gram of grape ash.

Similar to the standard for cider vinegar, this standard has recently been simplified by requiring only the acetic acid to comply with the limit, viz.: "not less than four (4) grams of acetic acid in one hundred (100) cubic centimeters (20° C.)" of the vinegar.

It will be noticed that the standard reads "juice of grapes." We have pointed out in connection with the apple vinegar standard the absurdity of insisting upon the use of straight apple juice (meaning first pressings only) for apple vinegar making, and in the present instance it is evident that the commission have overlooked the fact that a "second pressing," made by macerating grape pomace with water and repressing, is in common use abroad for vinegar making. Moreover, the alcohol in the above average wine yields 10.7 percent acetic acid upon full fermentation, and may show as high as 15 percent acetic acid, either strength being entirely too high for table purposes. A diluted wine or a standardized "second pressing" is necessary for table fruit vinegar making, if dilution of finished product is to be avoided; also, if the use of selected pure cultures of wine-vinegar

\* The author was called upon some time ago to analyze a grape juice concentrate containing 62.8 percent of reducing sugars.

bacteria is to ever become practicable, it is necessary that the "vinegar stock" should not be too alcoholic. Perold (*Centralblatt f. Bacteriologie*, 1909) has shown that only certain powerfully acidifying bacteria found in southern European wines can live in wines high in alcohol (12 to 14 percent by volume), and they are apt later to consume acetic acid and give a disagreeable aroma.

Perold found but one and usually a specific variety of acetic bacteria in each kind of wine. Certain forms when isolated give a particularly fragrant vinegar, with wines of suitable strength.

The process in general use for wine vinegar making is the Orleans process, somewhat similar to our own cask fermentation method, except that the "wine-vinegar stock" is added week by week in increasing quantities of from one-half to two and a half gallons until the original 20 gallons of vinegar is made up to about 40 gallons. Then 20 gallons of product are removed, and at the end of every following week about 2 gallons are removed and an equal volume of "vinegar stock" added. A properly prepared cask will serve for six or eight years; then it must be thoroughly cleaned of accumulated yeast, tartar and "mother vinegar."

The vinegar as first removed contains some unconverted alcohol, which, however, on ageing, is converted to acid or aids in forming esters, etc., of aromatic value. The writer has heard of several unsuccessful attempts at making wine vinegar by the generator process in this country, but he is of the opinion that, if properly conducted with not too strong an alcoholic "stock" the factory method in general use in America for making apple vinegar can be successfully used for grape vinegar also.

The data (Table 27) on some laboratory made white wine vinegars of known purity show the Federal standard limits to be fair, as concerns white wine vinegar. Formerly, it may be mentioned here, spirit vinegar was known as "white wine vinegar" in the United States. Much of the small amount of supposedly true white (and red) wine

Table 27. Analyses of White Wine Vinegar.

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	1.0129	1.0213	1.0175
	Percent		
Acidity (as acetic acid) .....	4.44	9.38	7.38
Total solids .....	1.38	3.19	1.93
Reducing sugars .....	0.06	0.46	0.22
Non-sugar solids .....			1.71
Ash (mineral residue) .....	0.16	0.69	0.32
Potassium bitartrate .....	0.07	0.36	0.17



vinegar sold here is adulterated in various ways, so much so that the reputable wine companies have not felt encouraged to go into the regular manufacture of a product that ought to have a large sale among our European-born population.

The analysis in Table 28 is given by Weigmann as the average of a number of analyses of red wine vinegar of known purity.

Table 28. Average Composition of Red Wine Vinegar.

Specific gravity .....	1.0143
	Percent
Acetic acid .....	7.79
Alcohol .....	1.19
Glycerin .....	0.14
Solids .....	0.86
Potassium bitartrate .....	0.06
Ash (mineral residue) .....	0.12

The above data (average values) show the Federal standard limits for "grape solids" and "grape ash" to be entirely too high for red wine vinegars as made abroad for centuries. The further fermentation of the alcohol in the above analysis would give a total of about 9.2 percent acetic acid, indicating a fairly strong grade of wines to have been used, which further shows the weakness of the wine vinegar standard, at least for red wine vinegars.

Wine vinegars are usually slightly levorotatory. It is stated that formic acid is a normal constituent of wine vinegar, a point that must be kept in mind when judging if a wine vinegar is adulterated with commercial acetic acid, by means of the formic acid estimation. Inositol is also another normal constituent and is valuable for distinguishing between wine and spirit vinegar.

### MALT VINEGAR

The most common vinegar of England, and one which is becoming well known and appreciated in America, is the product known as malt or beer vinegar. Just as the original and best beers were made from an infusion or wort extracted from malted barley, or a mixture of malted and unmalted barley, so are the best malt vinegars made entirely from malt, and unmalted barley in which the starch has been changed to sugars by the action of malt.

However, as is well known, much, if not most, of the beer of nowadays is brewed from a wort derived from the mashing of not only malt and various other cereals or cereal products, but from worts containing "glucose" ("brewer's sugar"). The Federal standard for

malt vinegar (Circular 136, U. S. Department of Agriculture) does not recognize the utilization of "glucose" in preparing a wort for conversion into malt vinegar, but provision is made for the utilization of cereals other than barley, providing the starch of the same has been converted to sugar by the action of malted barley.

In full the standard originally read as follows: "Malt vinegar is the product made by the alcoholic and subsequent acetous fermentations, without distillation, of an infusion of barley malt or cereals whose starch has been converted by malt, is dextrorotatory and contains in one hundred (100) cubic centimeters not less than four (4) grams of acetic acid, not less than two (2) grams of solids and not less than two-tenths (0.2) gram of ash, and the water soluble ash from one hundred (100) cubic centimeters of the vinegar contains not less than nine (9) milligrams of phosphoric acid ( $P_2O_5$ ), and requires not less than four (4) cubic centimeters decinormal acid to neutralize its alkalinity."

This has recently been simplified to require only that the acetic acid be "not less than four (4) grams in one hundred cubic centimeters (20° C.)" of the vinegar.

It is unnecessary, in connection with the malt vinegar standard, to go into a consideration of the chemistry of and legal requirements (standard) for beer. Calculations on high-grade malt vinegars, after allowing for a loss of acetic acid in the generator equivalent to 30 percent of the theoretical yield, indicate the original malt infusion to have contained close to the 14.8 grams (per 100 cc.) of solid substances in solution (about 65 percent of which is maltose) characterizing the so-called standard beer wort (specific gravity 1.057) of the British Inland Revenue Act. Worts intended for beer fermentation, however, although capable of being ultimately converted into malt vinegar need not be considered here, as the vinegar-yielding fermentations are conducted usually in separate establishments and with less care.

A properly prepared wort of barley malt alone will contain about 65 percent of the dry malt used, but malt alone is seldom, if ever, used. The best malt vinegars of England are prepared from mashing a mixture of barley malt and ungerminated barley, during which operation the enzyme diastase in the germinated barley (malt) acts upon the starch of both the germinated and unaltered barley to form the sugar maltose and a certain proportion of dextrin. Various other fermentations occur during the mashing stage, whereby soluble nitrogenous substances (peptones, amides, etc.) are formed

from grain proteins. Other cereals can be, and frequently are, substituted wholly or in part for the ungerminated barley, but the addition of fermentable sugars (glucose) to the liquid wort, or infusion resulting from mashing, should not be practised.

The alcoholic fermentation of the drawn-off wort consists principally of two enzyme-caused changes: First, the conversion of the maltose\* to dextrose (d-glucose), and then the conversion of the latter into alcohol and carbon dioxide by the enzyme zymase of the yeast. Both operations go on simultaneously, and from 100 parts of maltose about 51 parts by weight of alcohol is obtained theoretically. A standard malt wort (sp. gr. 1.057) would contain close to 9.1 percent of maltose, and according to the above statement would yield a malt vinegar stock or gyle containing 4.64 percent (by weight) of alcohol. This agrees well with the alcohol of English beer prepared from worts of standard specific gravity.

One hundred parts by weight of alcohol yields 120 parts of acetic acid in a well regulated generator fermentation, and the above strength alcoholic liquor thus fermented would figure out 5.57 percent acetic acid strength. The average acid strength of the eleven samples of pure malt vinegar reported in Allen's "Commercial Organic Analysis" was 5.5 percent, and three well-known English brands analyzed by the author also averaged 5.5 percent acetic acid.

It is probable that the use of generators in vinegar making originated in connection with the manufacture of malt vinegars; at any rate the acetic fermentation is practically always thus conducted, but at a much slower rate than in American cider vinegar making, which enhances the value of the product. In the Hill-Evans & Co. establishment at Worcester, England, sometimes a month is required to complete the acidification, the liquor being repeatedly distributed by pumps over the bunches of birch twigs by which the oxidizing fermentation is effected.

Malt vinegar ranges in specific gravity from 1.013 to 1.023; therefore, for practical purposes grams per 100 cubic centimeters can be read as percent. The proportion of solids is a little higher than in cider vinegar (but not 4 to 6 percent, as stated by Leach), and in addition to containing considerable nitrogenous matter, as explained above, it contains phosphates and frequently unconverted maltose and dextrin.

Malt vinegar is the first vinegar that we have considered so far in which water other than that found in fruit is legitimately used.

\* Maltose appears to be incapable of direct fermentation into alcohol.

Table 29. Malt Vinegar (14 samples.)

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
	Percent		
Acidity (as acetic acid) .....	2.88	6.61	5.50
Total solids* .....	1.68	4.23	2.75
Nitrogen .....	0.095	0.120	0.102
Ash † .....	0.22	0.57	0.44
Total phos. acid (P <sub>2</sub> O <sub>5</sub> ) .....	0.057	0.130	0.080
P <sub>2</sub> O <sub>5</sub> in soluble ash .....	0.001	0.012	....
Decinormal acid required for soluble ash....	3.2 cc.	24.9 cc.	12.1 cc.
Polarization ‡ .....	+0.6° V.	+2.9° V.	+1.7° V. §

\* Grams per 100 cc. † Residue after burning. ‡ 200 mm. tube. § Three samples only.

To make the original wort from the dry malt and other cereal products water is, of course, necessary, and as the natural mineral matter in waters from wells, etc., varies greatly in nature and quantity, it will be seen that any requirements as to the soluble ash of malt vinegar and its alkalinity, etc., are inadvisable. Thus, the use of a water especially rich in lime salts (gypsum) would tend to reduce the natural alkalinity of the ash, due to soluble carbonates, and the phosphoric acid in the ash might be rendered entirely insoluble.

The former standard limits for practically everything except total ash are violated by the above data on samples of malt vinegar of known purity. A requirement of at least 90 milligrams of nitrogen to 100 cc. vinegar would seem feasible, as the nitrogenous matter derived from the malted cereal is a characteristic and appears to vary within a comparatively small range. The dextrorotatory polariscopic reading is probably due to dextrin, coming from the malting of the starch in the grain. The writer (and Dr. Chapman in England) has shown that the polarization of malt vinegar is sometimes naturally levorotatory, due to certain levorotatory proteins remaining undecomposed, in sufficient proportions to overcome the dextrorotatory effect of the dextrin. Chapman thought that perhaps sometimes even the dextrin was completely fermented out during the preparation of the gyle, leaving mere traces of proteins to account for a slight levorotatory polariscope reading in the finished malt vinegar.

The use of commercial diastase for fermenting the cereal starch into malt sugar (maltose) might also be the cause of proteins remaining undecomposed in sufficient proportion to reverse the polarization due to dextrin. Malt vinegars also show small proportions of unfermented sugars, Baily reporting from 0.08 to 0.9 percent.

## SPIRIT AND SUGAR VINEGARS

From a chemical standpoint the vinegars we are now to consider are comparatively simple in their derivation, formation and composition; but with the steady increase in cost of the fruit-juice vinegars they have become very important commercial products. Spirit vinegar, for instance, is practically the only vinegar now used for pickling and the preparation of condimental compounds like prepared mustard, catsup, meat sauces, etc.

Spirit vinegar, distilled vinegar, or grain vinegar, as it is variously called, is, as the name would imply, the product resulting from the acetic fermentation of a weak alcoholic spirit distilled supposedly from an alcoholic fermented mash of malted or otherwise prepared cereal substances, but also frequently from fermented molasses or other sugar residues. The true sugar vinegars, however, have not undergone any distillation process, but are made directly by the acetic fermentation of an alcoholic fermented solution (syrup) of sugar, or glucose, or honey.

The Federal standard for spirit or distilled vinegar specifies it as the "product made by the acetous fermentation of dilute distilled alcohol, and contains, in one hundred (100) cubic centimeters (20° C.), not less than four (4) grams of acetic acid." In spirit vinegar "grams per 100 cubic centimeters" corresponds very closely to percent (by weight), which multiplied by ten gives us the customary "grain" system of acid measurement in use in trade circles. Thus 4 grams per 100 cubic centimeters is 4 percent, or 40 "grains"; 4½ percent would, of course, be 45 "grains," and 10 percent would be 100 "grains." The usual strength at which spirit vinegar is sold by the manufacturers is 90 "grains" (9 percent acetic acid), the product being reduced later to the desired strength by the addition of water. For table purposes, 4 to 4.5 percent acetic acid is sufficient, and it would be interesting to know officially how criminal a proceeding this dilution of the naturally prepared 9 percent vinegar to a lower strength before selling at retail is considered. The dilution of a naturally prepared 6 percent apple vinegar to the desired 4 or 4.5 percent is officially frowned upon unless plainly stated on the label; why should not the addition of water to naturally prepared spirit vinegar be similarly regarded? The reduction of a valueless 2 percent of gummy matter from the apple to 1.333 percent "apple solids" can not be the only explanation for the illogical exception.

The author has tested samples of genuine spirit vinegar contain-

ing as high as 12 percent acetic acid, and it is probable if the acetic bacteria characteristic of the strongly alcoholic wines of southern Europe were utilized in the generators that an acid strength as high as 15 percent might be obtained.

The specific gravity of spirit vinegar averages about 1.01, and in addition to aldehyde there is frequently present a little unconverted alcohol. The proportion of solids is insignificant and the polariscopic reading always zero. The natural color is a faint yellow, some samples being nearly colorless. The following maximum and minimum results may be of interest:

Table 30. Analyses of Spirit Vinegars.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Total solids .....	0.04	0.44
Ash .....	Trace	0.09
Acidity (as acetic) .....	4.05	12.00
Reducing sugars .....	0.02	0.09
Alkalinity of soluble ash (cc. N/10 acid required) .....	0.8 cc.	2.8 cc.

Spirit vinegar, in spite of its low price, is adulterated and sometimes entirely substituted by solutions of commercial acetic acid, which latter can be bought of a strength as high as 99.9 percent acetic acid. The concentrated acetic acid of commerce is called "glacial acetic acid." Diluted to proper strength it is sometimes more honestly sold as "imitation spirit vinegar," and owing to its close chemical similarity to spirit vinegar, perhaps even the term "artificial spirit vinegar" would be sometimes considered proper. Generally, however, the resemblance to the flavor of a good spirit vinegar is so poor as to justify only the prefix "imitation" or suffix "substitute."

The most important of the sugar vinegars is the product now being sold to considerable extent as "syrup vinegar." This results from the direct alcoholic and subsequent acetic fermentations of a sugar syrup (molasses can also be used, yielding a "molasses vinegar") of suitable strength, and if a dark-colored syrup be used (an over-heated, slightly caramelized syrup, for instance) a fine color can be obtained in the vinegar resulting therefrom. Two samples recently analyzed by the author showed about 0.25 percent of unchanged sucrose (also a little reducing sugar) and, as is characteristic of sucrose solutions, the direct polarization is slightly to the right (dextrorotatory) and levorotatory after inversion. The Federal standard requires at least 4 percent acetic acid in sugar vinegars. About 0.15 percent "ash" results on burning the 0.5 to 0.8 percent of total

solids. A compound of spirit and molasses vinegar is sold considerably, having a natural brown color.

The Federal standards also provide for a "glucose vinegar," the "product made by the alcoholic and subsequent acetous fermentations of solutions of starch sugar or glucose, (which) is dextrorotatory, and contains in one hundred (100) cubic centimeters (20° C.), not less than four (4) grams of acetic acid." This vinegar frequently smells and tastes of fermented starch. The small proportion of solid matter consists of unchanged glucose, particularly the dextrin portion, and like glucose solutions generally, it is strongly dextrorotatory as concerns polarized light, both before and after inversion. The ash is mainly lime salts present in the glucose as a result of the process of manufacture.

In the southwest several successful attempts have been made at making a vinegar from a solution of honey. Owing to a deficiency in nutrients, particularly nitrogen, potassium and phosphoric acid, for the yeast plant, it has been found advisable to add to the dilute honey solution a small proportion of certain chemical salts which, in conjunction with yeast cake, has been found to promote a rapid alcoholic fermentation. Several acceptable formulæ are available. The honey "wine" is then racked off, mixed with some good vinegar, or inoculated properly with "mother vinegar," and after an acetic fermentation of from four to six months at proper temperatures a very good honey vinegar is obtained.

#### MISCELLANEOUS FRUIT VINEGARS

Vinegars can also be made from other fruit juices than apple and grape. A very good vinegar has been made in the northwest from prunes, and experiments at making a pineapple juice vinegar have proven quite successful. Probably the generator process could be used in the manufacture of honey vinegar, thereby effecting a great saving of time, and also probably in the manufacture of pineapple and other new fruit juice vinegars.

Recently a client of the author's has made a very acceptable vinegar from the juice of the watermelon. This tested as shown in Table 31.

The Federal food standards have fixed no analytical limits, as yet, for these new fruit juice vinegars, but the U. S. Bureau of Chemistry has made a thorough study of the chemistry of orange and peach vinegars and, of course, the definition of such products would

Table 31. Watermelon Vinegar.

	Percent
Acidity (as acetic acid) .....	4.60
Alcohol (by volume) .....	0.20
Total solids .....	1.01
Reducing sugars .....	0.34
Non-sugar solids .....	0.67
Total ash .....	0.21

be similar to that for apple vinegar, i.e., the "product made by the alcoholic and subsequent acetic fermentation of the juice" of the particular fruit used.

In the *Journal of Industrial and Engineering Chemistry* for December, 1920, the Bureau of Chemistry describes two processes used to produce orange vinegar, one in a small way by a rolling barrel process, and the other on a commercial scale using the generator method. In the latter process, five different lots of oranges were used, two of sound fruit and three of frozen fruit. The details of procedure are too numerous to be given here and manufacturers interested should consult the original article or the U. S. Department of Agriculture. The orange vinegar made by the barrel process analyzed as shown in Table 32.

Table 32. Orange Vinegar (barrel process).

	—Grams per 100 cc.—		
	Lot 1	Lot 2	Lot 3
Total acidity (as acetic acid) .....	5.97	5.52	6.03
Volatile acid (as acetic acid) .....	5.09	4.52	5.06
Fixed acid (as citric acid) .....	1.03	1.16	1.13
Alcohol (by volume) .....	0.50%	0.39%	0.75%
Total solids .....	2.99	...	2.96
Total ash .....	0.48	...	0.47
Soluble ash .....	0.40	...	0.36
Alkalinity of soluble ash (cc. N/10 acid required)	45.1 cc.	...	40.8 cc.

Excepting the alcohol and the alkalinity of the soluble ash, the above results are in grams per 100 cubic centimeters, which correspond fairly close to percent by weight. The yield of acetic acid is good and is increased by approximately 1 percent of citric acid, the natural fruit acid of the orange, which, unlike the malic acid of apples, is not lost during the acetic fermentation and ageing. The flavor of the vinegar was characteristic and pleasant.

Of more interest commercially are the data on the orange vinegars made by the generator process. Table 33 gives the changes in composition, on two runs, from the fresh juice to the resulting vinegar.



Table 33. Orange Vinegar (generator process).

	Fresh Juice	Lot 4 Orange "Wine"	Orange Vinegar	Fresh Juice	Lot 5 Orange "Wine"	Orange Vinegar
	Grams per 100 cc.					
Total acidity (as citric acid)....	1.14	1.13	...	1.14	1.14	...
Total acidity (as acetic acid)....	...	...	4.74	...	...	4.70
Fixed acid (as citric acid).....	1.12	1.03	1.07	1.13	1.07	1.04
Volatile acid (as acetic acid)....	...	0.09	3.74	...	0.07	3.73
Total solids .....	13.39	3.64	4.34	13.49	3.43	4.02
Total sugars (after inversion)....	9.91	...	0.20	9.87	...	0.17
Alcohol (by volume) .....	...	5.73%	0.43%	...	5.75%	0.37%
Total ash .....	...	0.48	0.61	...	0.46	0.55
Soluble ash .....	...	0.38	0.44	...	0.37	0.41
Alkalinity of soluble ash (N/10 acid) ...	...	51.2 cc.	55.2 cc.	...	50.0 cc.	53.2 cc.

Compared with apple vinegars, these generator-made orange vinegars show low volatile acetic acid yield, but, as said above, the total acidity is brought up to an acceptable table strength by the approximately 1 percent of citric acid remaining in the finished vinegar. This is also shown to be the case in the analyses of four lots (three of them before and after ageing), made by the generator process (Table 34).

Table 34. Orange Vinegar (generator process).

	Lot 2 2 mos.	Lot 2 9 mos.	Lot 3 Fresh	Lot 4 Fresh	Lot 4 4 mos.	Lot 5 Fresh	Lot 5 4 mos.
Specific gravity (15.5° C.)	1.0209	1.0224	1.0277	1.0229	1.0240	1.0217	1.0225
	Grams per 100 cc.						
Total acidity (as acetic)...	4.74	5.02	4.91	4.74	4.98	4.70	4.91
Fixed acid (as citric acid)	1.00	1.00	1.20	1.07	1.07	1.04	1.04
Volatile acid (as acetic)...	3.79	4.08	3.79	3.74	3.98	3.73	3.93
Alcohol (by volume).....	0.36%	0.07%	0.03%	0.43%	0.34%	0.37%	0.26%
Glycerine .....	0.25	0.22	0.24	0.22	0.23	0.21	0.21
Total solids .....	3.82	4.08	5.26	4.34	4.50	4.02	4.12
Reducing sugars .....	...	0.22	...	...	0.29	...	0.24
Non-sugar solids .....	...	3.81	...	...	4.21	...	3.88
Volatile reducing substance	...	0.03	...	...	0.04	...	0.01
"Protein" (N × 6.25).....	...	0.75	...	...	0.61	...	0.56
Total ash .....	0.52	0.54	0.79	0.61	0.64	0.55	0.57
Soluble ash .....	0.37	0.38	0.50	0.44	0.47	0.41	0.42
Total P <sub>2</sub> O <sub>5</sub> in ash.....	0.045	0.046	0.053	0.039	0.042	0.035	0.036
Alkalinity of sol. ash* .....	44.0 cc.	48.0 cc.	64.0 cc.	55.2 cc.	57.2 cc.	53.2 cc.	54.0 cc.
Alcohol precipitate .....	...	1.06	...	...	1.12	...	0.95
Lead acetate test—all gave a very heavy precipitate.							

\* Decinormal acid required per 100 cc. vinegar.

It is interesting to note that the characteristic volatile reducing substance of apple vinegar (known as acetyl methylcarbinol) is practically absent in orange vinegar and that the proportion of total solids and non-sugar solids is decidedly higher than in apple vinegar.

A very interesting study of the "Value of Peaches as Vinegar Stock" is reported in the U. S. Bureau of Chemistry Circular 51, by

H. C. Gore of the Division of Foods. A small generator was used and well flavored vinegars resulted, which however did not retain any of the distinctive flavor of the peach and which remained persistently turbid. Filtration with modern accessories, such as "Filter-Cel," would probably have yielded clear products. The interested manufacturer should send for and consult the above-mentioned Circular 51.

Peaches are fairly rich in sugars and the different varieties do not differ much. Table 35 shows the range and average values of the juice from nine varieties used in the Bureau of Chemistry experiment.

Table 35. Composition of Peach Juice.

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity (17.5° C.).....	1.0508	1.0596	1.0539
		Percent	
Acidity (as malic acid) .....	0.63	0.85	0.75
Reducing sugars (as invert) .....	2.21	6.19	3.93
Sucrose (ordinary sugar) .....	3.50	7.15	5.87
Total sugars (as invert sugar).....	8.60	10.87	9.91

The average of 9.91 for total sugars is about 1 percent less than the average for American apple juices and the average acidity of peach juice is about 0.2 percent greater than that of apple juice. However, as in the case of apple vinegar, a considerable proportion of the natural fruit malic acid is lost during the manufacture of peach vinegar.

In the process used the peaches were pulped, leaving the stones therein, then fermented in loosely covered barrels or tanks and the fermentation was complete (at summer temperature) in three to four days. Pressing of the fermented pulp followed immediately and the peach "wine" flowed readily from the press, the ground peach stones apparently assisting the drainage of the press-cake. The yield of fermented juice was high, being above 80 percent of the ground fruit, and analyzed as shown in Table 36.

Table 36. Peach "Wine" or Peach "Cider."

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity .....	1.0076	1.0132	1.0107
		Percent	
Total acidity (as malic acid) .....	0.71	1.28	0.95
Volatile acid (as acetic acid).....	0.07	0.58	0.30
Fixed acid (as malic acid) .....	0.54	0.69	0.63
Alcohol (by weight) .....	3.52	4.40	4.07
Total solids .....	3.52	4.94	4.19
Reducing sugars (as invert sugar) .....	0.16	0.62	0.38
Non-sugar solids .....	3.32	4.32	3.81

The average alcohol yield corresponds to 5.1 percent by volume, which is practically the same as for American apple ciders, and the

proportion of solids is distinctly higher in peach "cider." The three samples of peach vinegar made from the nine batches of fermented peach juice gave in one instance as high an acetic acid yield as the average for apple vinegars, but the average of 4.81 percent, as a whole, is about 0.4 percent (4 "grains") below the average for apple vinegars. The three samples tested as shown in Table 37.

Table 37. Peach Vinegars.

	<i>Lot 1</i>	<i>Lot 2</i>	<i>Lot 3</i>	<i>Average</i>
Specific gravity .....	1.0161	1.0227	1.0231	1.0206
	Percent			
Total acidity (as acetic acid) .....	4.23	4.85	5.34	4.81
Volatile acid (as acetic acid) .....	3.89	4.78	5.21	4.62
Fixed acid (as malic acid).....	0.34	0.07	0.13	0.18
Alcohol (by volume) .....	0.25	0.25	0.03	0.17
Total solids .....	2.64	3.81	3.64	3.36
Reducing sugars (as invert sugar)....	0.44	0.68	0.84	0.65
Non-sugar solids .....	2.20	3.13	2.80	2.71
Total ash .....	0.30	0.58	0.58	0.49

Peaches are particularly subject to a brown rot caused by *Monilia*, which does not interfere with the alcoholic fermentation of the ground peaches, if not excessive, but which, however, does cause a large loss in fermentable sugars, and vinegar which was made from badly rotted peaches was deficient in acidity, and had disagreeable flavors and darkened quickly in the air.

In general it was found that peaches contain sufficient fermentable sugar for use as vinegar stock and that they can be successfully handled by the regular vinegar factory equipment.

Mention has been made of the possibilities of making a vinegar from raisins. This would bear somewhat the same relation to wine vinegar that dried apple vinegars bear to cider vinegar, if whole raisins were used. However, the proposition advanced was to leach the sugar from the seeder waste (mainly seeds), allow to ferment and distill a spirit for fermenting into vinegar. Such a product would be merely a "spirit" or "distilled" vinegar, which already is made from a variety of raw materials containing cheap sugar. The term "grain vinegar" should be distinct from the term "spirit vinegar" and applied only to vinegars made from spirits distilled from fermented cereal mashes and constituting a considerably higher grade vinegar.

#### DRIED APPLE VINEGAR

Early in 1925 "Notice of Judgment 12367" was issued, announcing the complete victory by the Government, in the U. S. Supreme Court,

on the misbranding of vinegar made from dried apple products as "Apple Cider Vinegar made from Selected Apples" ("Excelsior Brand," etc.). "Notice" after "notice" has since been issued, reporting subsequent convictions for similar offenses, most of them against the same manufacturer, who had the monumental self-confidence to contest the now famous, above-mentioned test case. Presumably these convictions are all for old shipments, made while the defendant was buoyed up with the confidence begot by a temporary victory (in the Circuit Court of Appeals) against the first lower court conviction.

The author, many years ago, taking the view that the term "apple vinegar" had a broader significance than the term "cider vinegar," argued before the then chief of the U. S. Bureau of Chemistry for the privilege of using the term "Apple Vinegar" for vinegar made from a water infusion of dried *whole* apples ("chops"). The comparative excellence of the samples submitted and the very close similarity in chemical data to that of cider vinegar, were admitted by the Bureau chief, and, in later years, the trade was given the privilege temporarily of so designating vinegar made from dried apple. But that did not satisfy the manufacturer whose conviction finally settled the question. Unlike the client for whom the author had argued the matter, this manufacturer must go to the limit of absurdity, must so try the patience of the Government officials by his insistence upon using the term "cider vinegar," for the dried apple product, that a Supreme Court decision resulted and a Food Inspection Decision was issued restricting both the terms "cider vinegar" and "apple vinegar" to vinegars made from the juice of fresh apples only.

The following excerpt from the Supreme Court decision is worth reproducing, even at this late day, as it presents the essential facts of the controversy in a "nutshell." How any Circuit Court of Appeals came to look at the matter differently is a mystery. It reads as follows:

"The statute is plain and direct. Its comprehensive terms condemn every statement, design, and device which may mislead or deceive. Deception may result from the use of statements not technically false or which may be literally true. The aim of the statute is to prevent that resulting from indirection and ambiguity, as well as from statements which are false. It is not difficult to choose statements, designs, and devices which will not deceive. Those which are ambiguous and liable to mislead should be read favorably to the accomplishment of the purpose of the act. The statute applies to food, and the ingredients and substances contained therein. It was enacted to enable purchasers to buy food for what it really is. *United States v. Schider*, 246 U. S. 519, 522; *United States v. Lexington Mill Co.*, 232 U. S. 399, 409; *United States v. Antikamnia Co.*, 231 U. S. 654, 665.

"The vinegar made from dried apples was not the same as that which would

have been produced from the apples without dehydration. The dehydration took from them about 80 per cent of their water content—an amount in excess of two-thirds of the total of their constituent elements. The substance removed was a part of their juice from which cider and vinegar would have been made if the apples had been used in their natural state. That element was not replaced. The substance extracted from dried apples is different from the pressed-out juice of apples. Samples of cider fermented and unfermented made from fresh and evaporated apples, and vinegar made from both kinds of cider were submitted to and examined by the District Judge who tried the case. He found that there were slight differences in appearance and taste, but that all had the appearance and taste of cider and vinegar. While the vinegar in question made from dried apples was like or similar to that which would have been produced by the use of fresh apples, it was not the identical product. The added water, constituting an element amounting to more than one-half of the total of all ingredients of the vinegar, never was a constituent element or part of the apples. The use of dried apples necessarily results in a different product.

"If an article is not the identical thing that the brand indicates it to be, it is misbranded. The vinegar in question was not the identical thing that the statement, 'Excelsior Brand Apple Cider Vinegar made from selected apples' indicated it to be. These words are to be considered in view of the admitted facts and others of which the court may take judicial notice. The words 'Excelsior Brand,' calculated to give the impression of superiority, may be put to one side as not liable to mislead. But the words, 'apple cider vinegar made from selected apples,' are misleading. Apple cider vinegar is made from apple cider. Cider is the expressed juice of apples and is so popularly and generally known. See *Eureka Vinegar Co. v. Gazette Printing Co.*, 35 Fed. 570; *Hildick Apple Juice Co. v. Williams*, 269 Fed. 184; *Monroe Cider, Vinegar & Fruit Co. v. Riordan*, 280 Fed. 624, 626; *Sterling Cider Co. v. Casey*, 285 Fed. 885, affirmed 294 Fed. 426. It was stipulated that the juice of unevaporated apples when subjected to alcoholic and subsequent acetic fermentation is entitled to the name 'apple cider vinegar.' The vinegar in question was not the same as if made from apples without dehydration. The name 'apple cider vinegar' included in the brand did not represent the article to be what it really was; and, in effect, did represent it to be what it was not—vinegar made from fresh or unevaporated apples. The words 'made from selected apples,' indicate that the apples used were chosen with special regard to their fitness for the purpose of making apple cider vinegar. They give no hint that the vinegar was made from dried apples, or that the larger part of the moisture content of the apples was eliminated and water substituted therefor. As used on the label, they aid the misrepresentation made by the words 'apple cider vinegar.'

"The misrepresentation was in respect of the vinegar itself, and did not relate to the method of production merely. When considered independently of the product, the method of manufacture is not material. The act requires no disclosure concerning it. And it makes no difference whether vinegar made from dried apples is or is not inferior to apple cider vinegar.

"The label was misleading as to the vinegar, its substances, and ingredients. The facts admitted sustain the charge of misbranding.

"Judgment reversed."

As to other ingredients than apple water being removed by drying the apple products (frequently only cores and skins from the evaporated apple industry) testimony was not offered, but it could have been pointed out that in the drying process the volatile esters, to which the apple odor is due, were necessarily lost.

Dried apple vinegar, made from "chops" (small, *whole* apples, not merely cores and skins), is an excellent product, which, even though

now deprived of the privilege of being called "apple vinegar," can still find a market. But illogical obstinacy has not helped it any.

The author's argument in favor of the privilege of calling it "apple vinegar" was based upon the fact that dried ("evaporated") apples are extensively used in the manufacture (in the home and in the restaurant trade) of apple sauce and apple pie, for which no one has ever suggested the terms "dried apple sauce" or "dried apple pie."

#### HINTS ON VINEGAR BUYING

In the food trade, as in any other field of activity, new conditions call for new methods and precautions. Vinegar adulteration, as once practised, has changed materially. Apple jelly and dilute acetic acid, or spirit vinegar, once were considered a shrewd adulteration, but are now seldom resorted to. Allowing apple pomace to ferment, wetting with water and repressing was once considered a legitimate method of obtaining more apple "juice"; now the fermenting of pomace is officially frowned upon (as yielding a "decomposed" apple juice) and water added at the pressing stage must be admitted on the label just as much as if added to the finished vinegar.

There is no need of going through the whole list of changes in the style of adulterations practised; in fact adulterators are always a little ahead of official inspection chemists, as the latter must first discover the new style of adulteration being practised before they can exert any control of it. Briefly, therefore, we will merely give hints to buyers, etc., as to what to be on the lookout for, and other details, dealing with quality and grade, in addition to legal purity.

Perhaps the first thing to be on guard against is the presence of vinegar "eels." These render products turbid and convey a very unfavorable impression when discovered by the consumer. The customer may be temporarily interested in watching the aimless wriggling of the tiny creatures, but when he buys vinegar for a cruet on the table, he is not interested in getting an aquarium incidentally. Worst of all, vinegar "eels" cause a steady decrease in the acidity and general quality of vinegar, as they feed upon constituents in the vinegar and breed fairly fast.

The second precaution is to guard against the incipient decomposition flavor. Vinegars made from clean, sound apples by clean methods will retain their virgin flavor (or improve on it) for many months. Vinegars made from "culls" (partially rotten and dirty apples), or a good "vinegar stock" run through a generator infected with foreign

micro-organisms, will soon show signs of a progressive deterioration and spoilage; and after a varying interval of time will become actually offensive in flavor, appearance and odor. In fact, infected vinegars can lose character and acid strength so steadily as to ultimately become actually alkaline in reaction. A number of occasionally infecting bacteria, etc., rapidly consume the acetic acid of vinegar.

If the buyer will but let a submitted sample of vinegar stand in a fair place (not too hot, nor too exposed to air by opening often) for a week or so, he can easily judge whether decomposition is taking place and an experienced buyer can detect even the first (incipient) changes along these lines.

Probably the next important item is acidity, as this is mainly the basis of price adjustments and constitutes especially the "strength" of the vinegar in popular parlance. To be sure, we should look for strength of apple flavor (or grape flavor in a wine vinegar, etc.) as well as acidity, but whereas the former must be judged largely by organoleptic methods (nose, tongue, etc.) we have exact chemical tests for determining the acidity. The author, long ago, took the regular official acidity testing method and put it in an exact, very easy, safe form for a layman to use, so that even a simple laborer in a factory can get the same exact result that the most experienced official chemist would report.

The most important thing to remember about the acidity of a vinegar is that most of the vinegar shipped is "reduced" (diluted) vinegar and is sold as near to the 4 percent (40 "grain") minimum limit of the legal standard as the shipper can judge it. The 4 percent limit was never intended as a selling standard, but it has become such. It was fixed as a *legal minimum* below which no normal vinegar would ever naturally go. Vinegar was supposed to be sold up around an *average* acidity strength (between 4.5 percent and 5.5 percent) and 4 percent was fixed upon as a figure below which the slightest deficiency warranted a prosecution. Thus we have the vinegar trade using as a selling standard a *legal minimum* standard, below which any test that an official inspection chemist feels sure of, warrants a prosecution. This is a dangerous proposition and calls for very exact testing, both as to method used and experience in the use of that method. The author has always advised his clients (even those using the Brooks Official Acidity Tester referred to above) to sell, after carefully testing, at least 4.2 percent (42 "grains") and any buyer who does not know that his vinegar shows at least that strength is inviting trouble for himself and his customers, the retail grocers. Four and five-

tenths percent is an acceptable "table strength" and should supersede the present dangerous selling standard (4 percent) now being used. Wine and malt vinegars naturally average higher than cider (apple) vinegar and are usually sold at their average strength, but for some reason the cider vinegar shippers prefer to curtail the production and sale of apple cider vinegar by selling some water instead at a lower price.

The next thing for the buyer to guard against is the substitution of dried apple vinegar for cider (apple) vinegar made from fresh juice. If unsulfured dried apples (or cores and skins) were used and the same proportion of water as originally present was restored, the product would be a hard thing to identify by chemical data, but, of course, the original volatile "bouquet" of the fresh juice is lacking (due to loss of apple esters during drying) and an expert buyer can usually detect the difference. The chemical detection is at present based mainly on the presence of sulfates (coming from the sulfur), or of barium when the latter has been used to get rid of the sulfur. Of course, all up-to-date buyers now know that the Government finally won the erstwhile celebrated case and that vinegar made from dried apple products cannot be called cider or apple (without prefix "dried") vinegar.

Other adulterations, many of them quite shrewd and scientific, are in use, and to detect these the buyer must depend upon an experienced vinegar or food chemist. The analysis and the interpretation of analytical data of vinegars is a proposition calling for much experience, and to send a sample to the nearest chemist, irrespective of his specialty, is usually a fee thrown away.\*

In spirit vinegars, the buyer should distinguish between those made from cereals (grain vinegar) and those made from fermented molasses or other sugar residues, yet entitled to the name spirit (or distilled) vinegar. The experienced buyer can tell these apart by odor, especially after the acetic odor has been diluted or neutralized. Grain vinegar is a superior product.

#### VINEGARS VS. ACETIC ACID

The essential principle involved in the manufacture of any kind of vinegar is fermentation. It was a fermented product in the first place, always has been, and must be regarded henceforth as the prod-

\* It should be remembered that the legal standard for apple vinegars now fixes no analytical limits (except for acidity) to be tested for, but leaves it to the chemist to decide from a study of any data he may determine, whether the legal definition of cider vinegar has been complied with.



uct of fermentation, if the basic principles of food control are to prevail. Therefore any use of the term vinegar in connection with acetic acid solutions not derived from fermentation, is historically, legally and scientifically incorrect.

No self-appointed "Congress" of food manufacturers or officials, whether meeting in Geneva or Timbuctoo, can alter the facts of the case, nor make the terms "wood vinegar" or "acetic acid vinegar" proper in any sense. The word itself is derived from the French for wine, a product resulting from the alcoholic fermentation of natural sugars in fruits and other vegetable products. Thus we have apple wine (cider), grape wine, low wines (from alcoholically fermented mashes), cereal wines (gyle from fermented worts), honey wine, orange wine, blackberry wine, elderberry wine, etc.

In every one of the wine or wine-like "stocks" used for conversion into vinegars (by acetic fermentation) there is involved the principle of alcoholic fermentation. It would be just as logical to call a solution of synthetic alcohol a wine as to call a solution of acetic acid a vinegar merely because it contains some acetic acid. Tomatoes cannot be called oranges simply because each contains citric acid.

The acetic acid of a sour (acetic-fermented) wine is probably the oldest recognized acid and was for centuries associated with the idea of a vinegar, hence when acetic acid was also identified as one of the products resulting from the distillation of wood, the term "vinegar" was incorrectly used to designate the acid. There is no evidence that any one considered the wood-distillate acid a vinegar for condimental purposes, however. The only idea of a vinegar prevailing at that time was a wine or wine-like product which had turned sour. This alone would settle the question in a court of law, yet we still find interested parties trying to have the dilute purified acid, obtained from the distillation of wood or synthetically made from carbides, regarded as a vinegar!

A weak solution (5 to 10 percent) of commercial acetic acid will furnish acidity and nothing else, but in every vinegar, no matter how humble, we have present considerably more than mere acidity; we have present the other flavoring substances which constitute the condimental value, flavoring substances formed by natural processes and characteristic of the condiment.

There is perhaps no more conclusive way to demonstrate the differences between a vinegar and a mere solution of acetic acid than to list some of the other substances found in different vinegars and not present in a solution of acetic acid, and to the combined taste and

odor of which, the condimental value of a vinegar (aside from mere acidity) is due.

The vinegar which has been most extensively analyzed is apple or cider vinegar and in addition to acetic acid we find therein small but essential proportions of alcohol, glycerin, sugars, pentosans, tannin, pectin, gums, malic acid, lactic acid, ethyl acetate and other esters of flavoring value, mineral salts (phosphates, malates, etc.), acetylmethylcarbinol and several aldehydes. It is to the combined action of all these various ingredients that the flavoring and general dietetic value of apple or cider vinegar is due, and is there any one so bold as to say a 5 percent solution of acetic acid will take its place?

Likewise grape vinegar, or "wine vinegar" as better known, is an equally complicated substance containing, besides acetic acid, small but essential proportions of alcohol, glycerin, sugars, including inositol, tannin, gums, cream of tartar, succinic acid, formic acid, methyl-acetol, acetaldehyde, ethyl acetate and other esters, phosphates and other mineral salts.

One of the most characteristic, distinctively flavored vinegars is malt vinegar. In malt vinegar there are present various final derivatives of the original proteins of the cereal, formed during the malting, mashing and successive fermentations, which partly account for the characteristic flavor. Altered proteins are sometimes present and intermediate protein derivatives such as peptone and complex amino compounds. There is also the usual alcohol, glycerin, sugars, dextrin and other gums, esters formed during ageing, phosphates and other mineral salts, and ammonium salts, when the fermentation of the proteins has been very complete.

Thus we could go through the complete line of different fruit vinegars and list various constituents, other than acetic acid, which give a characteristic condimental value to each vinegar. Even the vinegars made from fermented sugar solutions ("sugar wines"), such as honey, cane syrup and "glucose," contain their quota of alcohol, glycerin, residual sugar, gums, esters and mineral salts.

Spirit vinegars, made from the "low wines" distilled from alcoholically fermented cereal and sugar mash, are less complicated in constitution than vinegars which are made direct from alcoholically fermented juices, syrups and infusions, but even here we find various volatile ingredients, other than acetic acid, which give a flavor to spirit vinegar which no solution of acetic acid can duplicate. Unchanged alcohol is present which in time forms ethyl acetate and other esters of noticeable flavoring value. The aldehydes and higher alcohols, con-

stituting the so-called congeneric products of the distillation of an alcoholic fermented cereal mash or sugar solution, will be present and traces of gums and salts are carried over mechanically during the distillation of the "low wines."

Thus it will be seen that the humblest real vinegar, whether a spirit vinegar or a simple syrup vinegar, is considerably more than a mere solution of acetic acid; and to substitute such a mere chemical, partial imitation of vinegar for the real thing is not only a fraud but is an insufficient substitute. One has only to visit various low grade pickling and prepared mustard plants to see how much of this substitution of acetic acid for legally required vinegar is going on.

When a food standard, as for example the standard for prepared mustard and tomato catsup, specifies vinegar as one of the permitted ingredients, some kind of *vinegar* is meant, not an acetic acid solution of equivalent acid strength. Vinegar is present in such compound food products for its bouquet as well as acidity and the pickle-maker who is substituting a mere acid solution is weakening the value of his product much more than the slight saving on the cost of real vinegar warrants.

Acetic acid has been used with some success in making an acid extract of spices for flavoring catsups and other food products, but even here a strong (12 percent) spirit vinegar could be used to extract the flavoring oils, etc., from the spices. Or the spice oils can be purchased as such and used direct in some instances. The value of most spices depends upon certain essential oils found therein. Thus cinnamon or cassia oil and clove oil represent all the flavoring value of those several spices.

## Chapter III.

### Interpretation of a Vinegar Analysis.

In the early days of food inspection, the official analysis of a vinegar consisted of a test for the degree of acidity (with an occasional test for substitution of a mineral acid) and in the case of fruit vinegar an estimation of the proportion of total solids and ash (residue left upon burning the total solids) with some consideration of the ratio of the last two items to each other. In the case of malt vinegar a trifle more lengthy and conclusive analysis was in vogue, especially in England.

#### CIDER OR APPLE VINEGAR

"Apple vinegar" was formerly officially allowed as the designation for vinegar made from dried apple products, while the name "cider vinegar" is very properly restricted to the product made from fresh apple juice. The items tested for in the two vinegars are identical, however, as the main purpose in each case is to determine if apple material and apple material only (aside from any added water) has been used in the process of making. Dried apple vinegar is identified mainly by a test for sulfates, coming from the sulfur fumes used in bleaching and preserving the dried apple material.

The official analysis of cider (or apple) vinegar is now a quite lengthy and intricate affair, requiring much expert official analytical experience and, most of all, an extensive knowledge and experience in the legal chemistry of apples, apple juice, cider and cider vinegar, in order to properly interpret the analytical data, after it has been determined. It is usually in the interpretation of the data where many chemists (including some State and Government chemists) fall down, although mistakes in the rather difficult analysis itself are not uncommon. For example, a recent State "campaign" condemned hundreds of pure cider vinegars because the polarization (polariscope reading on the clarified vinegar) was slightly plus instead of minus, as a pure cider vinegar should be. This happened because the state analyst had blindly followed certain directions for clarifying given in the A. O. A. C. official methods (generally used in State and Federal food

inspection analysis) without being aware that an obscure note in the proceedings of the A. O. A. C. had pointed out that the use of a lead salt for clarifying cider vinegars, previous to taking polariscope reading, sometimes reversed the reading. The author pointed this out to the food commissioner and the campaign suddenly ended. The faulty method is still to be found in the A. O. A. C. official methods, the referee's criticism (in the obscure note) being apparently forgotten. By using the proper clarifying reagent, the correct reading is easily and correctly obtained. It is a very important test as a true plus reading is considered good proof of the use of commercial glucose, or unfermented sucrose, to increase alcohol yield and subsequent acetic acid strength.

The various analytical items will be discussed in the order as first given in the official and tentative methods\* of the Association of Official Agricultural Chemists ("Analytical" would be more appropriate than "Agricultural"), popularly known as the A. O. A. C. The methods and incidental data determined are the results of a thirty year "labor of love" (of science) on the part of poorly paid, busy official chemists and they have put the United States in the forefront in food inspection work. The author, as a former referee in the association, hesitates to laud the great work as much as it deserves, and will leave it to some more disinterested posterity. The same association, through its permanent committee on food standards (chairman of which was Dr. Wm. Frear of Pennsylvania, with whom the author is proud to have once been associated), has collected the data for and issued the majority of the official standards for food products proclaimed by the various Federal and State authorities.

**Alcohol.** The first item of analytical consequence in a cider vinegar analysis is the alcohol determination. It is a measure of the completeness of the acetic fermentation and in a properly made vinegar will not exceed a few tenths of one percent. Higher results indicate incomplete acetification in the generators, or the addition of vinegar "stock" (hard cider, etc) to finished vinegar, without allowing time for spontaneous fermentation in barrels later. Some States allow the alcohol left in vinegar to be counted towards the degree of acidity (in terms of acetic acid) required by the State standard. This is a sop to careless rural vinegar makers, as the consumer buys vinegar for its acid content and not with the idea of keeping it six months until all alcohol has changed to acetic acid. It thus happens that vinegar is sometimes found to have increased in acidity during stor-

\* *J. Assoc. Official Agri. Chem.*, vol. II, No. 2.

age, and State chemists have passed vinegars, which, if tested immediately after collection, would have been found below the low required minimum for acidity.

**Glycerol.** Next after the determination of alcohol in the official methods of the A. O. A. C. comes the determination of glycerol, or as better known, glycerin. Glycerol is one of the by-products of the alcoholic fermentation of fruit juices, succinic acid being another. Pasteur estimated that from 100 parts of sugar in a fruit, 48.5 parts of alcohol (by weight), 46.6 parts of carbon dioxide and about 3.3 parts of glycerol could be obtained. Kulisch reported from 0.38 gram to 0.59 gram per 100 cc. of glycerol in ciders, the ratio of glycerol to alcohol being approximately 1 to 10. Evidently some glycerol is lost during the subsequent acetic fermentation of a vinegar stock (or cider) as the glycerol content of cider vinegars, as reported by the U. S. Bureau of Chemistry, ranges from 0.24 gram to 0.46 gram per 100 cc. Under certain circumstances the acetic acid-forming bacteria act on glycerol forming carbon dioxide and water, and various other fungi and conditions are known to destroy glycerol in vinegars more or less completely.

Samples which are made under good control will probably show the proportion of glycerol that the Government chemists claim should be present, but it has always seemed to the writer that officials should go slow in basing a vinegar prosecution solely on a low glycerol content, in view of the fact that there is such a variety of possibilities of the glycerol being lost naturally. As spirit or distilled vinegar contains no glycerol, a low glycerol content has often been considered by official chemists to prove the addition of such an adulterant or the use of commercial acetic acid and water. There are other analytical items which will also prove such sophistications, such as the percent of volatile reducing substances (practically absent from spirit vinegar) and formic acid, practically always present in commercial acetic acid; therefore, there is no need or logic in basing a prosecution on the single questionable basis of low glycerol content, as has been done.

Moreover, the glycerol determination is a very lengthy and uncertain affair, even in the hands of experts, and the value not at all commensurate with the time and labor involved. In a factory laboratory it would be almost out of question to make the test with any degree of regularity, unless a big force of chemists were employed.

**Total Solids.** The next test is that for the proportion of total solids, which the former Federal standard for apple or cider vinegar says should be not less than 1.6 gram per 100 cc., or practically 1.6 per-

cent "apple solids." The range on pure samples, variously reported in the literature, is from 1.2 percent to as high as 4.5 percent, the average being 2.4 percent for natural undiluted cider vinegars. The maximum reported is, of course, from a vinegar where considerable sugar was left unchanged when the acetic fermentation superseded and checked the alcoholic fermentation. The "apple solids" are composed of sugars, gums, fruit acid, mineral salts, tannin, glycerol and pentosans mainly, and most of these items will be considered separately. The more expertly and completely the alcoholic fermentation is carried out, the lower the solids will be, hence high solids are no sign of quality, but rather the opposite. Solids are also lost during ageing.

**Sugars.** The next item of the legal purity analysis of a cider or apple vinegar to be considered, is a measure of the sugar, together with another (volatile) substance, which was formerly measured with and as sugar, thus making the old data on the sugar content of vinegar somewhat too high. This last fact probably explains how the original standard for cider vinegar allows 50 percent of the total solids to be "reducing sugars." In fact, in a properly made vinegar, the "reducing sugars" (calculated as invert sugar) will range between 10 percent and 25 percent of the total solids. The reducing sugars themselves range from 0.11 percent to as high as 1.1 percent of the vinegar itself (in seventy-five samples of known purity) and are composed of sugars having the property of reducing an alkaline copper salt solution, by which test they are measured. In the apple juice at least three different sugars are present, i.e., sucrose (ordinary sugar), d-glucose (dextrose or "grape sugar") and levulose or "fruit sugar," the latter having a levorotatory polarization. In the alcoholic fermentation, the sucrose soon disappears, together with most of the d-glucose, according to how soon an acetic fermentation gets started and checks the alcoholic fermentation. More than 0.5 percent acetic acid will retard the alcoholic fermentation considerably and Lafar showed that of fifteen varieties of yeast, only three were able to cause alcoholic fermentation when the acetic acid present exceeded 1 percent.

The sugar which seems to be utilized slowest is the levulose and this, together with traces of d-glucose (about one-fifth of the total reducing sugars in vinegar), never does fully disappear, the amount left in the vinegar depending upon how soon a restraining proportion of acetic acid develops during the alcoholic fermentation.

Therefore, a high sugar content in the vinegar, with a resulting high total solid content, is not an index of quality, but merely an index of a carelessly controlled alcoholic fermentation. Thus is mani-

fested the absurdity of fixing a high legal limit (2 percent for example) for solids in cider vinegar, as it will rule out many carefully fermented pure products and pass carelessly made ones and those deliberately reinforced with apple jelly, etc. A premium on carelessness and dishonesty, as it were, and absolutely unnecessary as other data will easily show dilution with water.

The test we are now considering estimates the proportion of "total reducing substances before evaporation." This, as said above, includes, in addition to reducing sugars (levulose with traces of d-glucose), a volatile substance capable of reducing alkaline copper salt solutions and known as acetylmethylcarbinol. Formerly this was measured as reducing sugar, because it reduced the alkaline copper salt solution, but now the analyst, after estimating the "total reducing substance," as called for in the test we are considering, evaporates another quantity of the vinegar to dryness and repeats the test. This last test gives the actual reducing sugars (usually expressed as invert sugar, although in malt vinegar it would be expressed as d-glucose or dextrose) and a differentiation of the levulose and any small amount of d-glucose can be made later if desired.

The difference (expressed as invert sugar) between the total reducing substances before evaporation and after evaporation is a measure of the "volatile reducing substance," recently identified as acetylmethylcarbinol. This item is quite a valuable item, as cider or apple vinegar contains fairly definite amounts of the volatile reducing substance while spirit vinegar contains mere traces if any and diluted acetic acid the same.

In cider or apple vinegar the proportion of this volatile reducing substance, expressed as invert sugar for sake of convenience, ranges from 0.14 to 0.34 percent in vinegars as generated, and from 0.10 to 0.29 percent when reduced to a 4 percent acetic basis. It appears to be formed during the acetic fermentation, as "hard" ciders and wines are reported as containing mere traces, if any.

The difference between the total solids and the actual reducing sugars is the rather important analytical item known as "non-sugar solids" and it includes all the items which are constant (excepting the fruit acid) and not dependent upon the degree of carefulness in fermentation, as are the sugars. Older results for this item are untrustworthy as the reducing sugar data included the volatile reducing substance, and therefore on subtracting an unduly high sugar value from the total solids an unduly low value was obtained for non-sugar solids,



resulting in unwarranted allegations of dilution with water and prosecutions therefor.

The Federal inspection chemists have been rather dogmatic on the question of how much non-sugar solids a genuine cider vinegar should show, claiming it should not be below 1.25 percent. The average pure vinegar will show from 1.2 percent to as high as 2.9 percent non-sugar solids, the average being about 1.9 percent in undiluted products, but there are bona-fide cases of going below even 1 percent. Messrs. Hartman and Tolman, two U. S. Bureau of Chemistry chemists at the time, conducted an investigation on rotating generator-made vinegar from cider of "stock" stored a year and found non-sugar solids as low as 1.09 percent, and the author knows of a case where a vinegar, from stored very "dry" cider, in which all fruit acid (malic acid) had fermented out (as surely happens in time), showed only 0.95 percent non-sugar solids. During storage of the cider there is a precipitation of pectin and gums, which in the investigation mentioned above caused a 48 percent loss of non-sugar solids, and this, with the sure disappearance of malic acid, will easily explain non-sugar solids values considerably less than the 1.25 percent looked for by official chemists. The main constituents of the non-sugar solids are the mineral salts (to be considered under the item "total ash"), gums, tannin, pectin, etc. High non-sugar solids would be due to abnormal proportions of the latter items, together with an unusual proportion of fruit acid (malic acid) remaining unchanged.

**Sucrose, Dextrin, etc.** Sometimes it is desirable to make another reducing sugar estimation after "inverting" the evaporated vinegar. This is for the purpose of estimating any starch, dextrin or unchanged sucrose (ordinary sugar) that may be present, although it will probably include traces of other substances which are converted into copper reducing substances by inversion. The process of inverting consists of heating with mineral acid whereby starch, dextrin or ordinary sugar are changed into reducing sugars. Thus any noticeable increase in the proportion of reducing sugars after inverting the evaporated vinegar will indicate the addition of starch, dextrin (from glucose for example) or ordinary sugar, for building up solids, or increasing alcohol yield in earlier stages of vinegar adulteration. It is possible that the mere heating (in presence of natural acetic acid of vinegar) during the evaporation of the sample, will convert, or invert, at least, any ordinary sugar present, into reducing sugars. This may explain certain very high results in the published data on reducing sugars in vinegar, for which the former Federal standards makes such an unduly

high provision. An honest, well made cider or apple vinegar contains a quite small proportion of reducing sugars before or after inversion and correspondingly low total solid content.

**Lead Precipitate.** The next test given in the official testing methods of the A. O. A. C. is a qualitative one only, i.e., the precipitate given by the addition of about 2 percent of a 20 percent lead acetate solution to the vinegar. The "lead precipitate" was formerly regarded as an index of the fruit acid of the apple juice (malic acid) and was considered a very valuable test in the olden days of food inspection. To be sure, a pure apple product vinegar will give a medium heavy precipitate with lead acetate solution, but it is due more to presence of gums, color and tannin than to fruit acid; in fact, in well aged vinegar the malic acid is practically all fermented out, yet a characteristic test with lead acetate solution is obtained. The precipitate frequently does not settle out at once and inexperienced official chemists have hastily made the test, obtained only an apparent turbidity and, immediately throwing away the solution in the test tube, have condemned the sample forthright. If they had let the test tube stand a little while they would have seen the "turbidity" coagulate into a characteristic precipitate, leaving a very pale brown or grey clear liquid above. If the upper layer of more or less clear liquid is a distinct brown, it indicates the presence of caramel or burnt sugar coloring, more surely than some of the regular tests for caramel color.

Attempts have been made to give a quantitative value to the lead precipitate test, by estimating the amount of lead used up, similar to the so-called "lead number" in vanilla extract analysis, but not enough data, or understanding of various conditions affecting the result, are available to make it decisive to any degree of certainty. The customary way, as yet, is to report as "turbid" or "light," "normal," heavy" or "very heavy" precipitate, noting also, if desirable, the color of the upper layer of liquid.

**Polarization.** Next is the test for polarization. This is a quite important test, it being the nature and extent of the reading given on the polariscope sugar scale (Ventzke scale) when a ray of polarized light is allowed to pass through a 200 millimeter tube of the properly clarified vinegar. Various sugars, gums, proteins (as in malt vinegar), essential oils and certain fruit acids (for instance the tartaric acid in grapes, wines and wine vinegar) have the property of rotating the ray of polarized light to the right (+) or left (—), more or less in proportion to the percentage of the sugar, gum, protein, etc., dissolved in the liquid in question, vinegar in this case.

Fresh apple juice, as previously explained, contains three different sugars in appreciable amount, i.e., sucrose (ordinary sugar), d-glucose (dextrose or "grape sugar") and levulose or "fruit sugar." The first two are dextrorotatory (i.e., they rotate the polarized light ray to the right (+), while the levulose or "fruit sugar" is levorotatory, giving a left-handed (—) reading on the polariscope sugar scale. A mixture of equal parts of dextrose and levulose is also formed when sucrose (ordinary sugar) is "inverted" by heating with acids. As the levorotatory effect of the levulose is more powerful than the dextrorotatory effect of the dextrose, the above mixture of the two, called "invert sugar," has a distinct levorotatory reading. The average apple juice contains about twice as much (7.2%) reducing sugars, as it does sucrose (3.4%), and, in apple juice, the proportion of levulose is over twice as much as the dextrose. Hence apple juice is strongly levorotatory in its effect on the ray of polarized light, averaging about  $-18^{\circ}$  (Ventzke sugar scale) in a 200 millimeter observation tube.

During the alcoholic fermentation the sucrose quickly disappears and also most of the dextrose (d-glucose), but the levulose ("fruit sugar") persists in small but distinct proportion to the end of the acetic fermentation and being considerably more powerful optically than the traces of dextrose remaining in the final vinegar, the natural polariscopic reading of a true cider or apple vinegar is always levorotatory (—) provided the proper clarifying agent has been used, when preparing the vinegar for the test.

Hard ciders range from  $-0.09^{\circ}$  to  $-2.64^{\circ}$  Ventzke, averaging  $-1.34^{\circ}$ , in the 200 millimeter observation tube, while the vinegar will range a trifle higher, viz.:  $-0.2^{\circ}$  to  $-3.6^{\circ}$ , average  $-1.4^{\circ}$  Ventzke, due to a further loss of dextrose and also perhaps some concentration during acetic fermentation.

The former Federal standard for cider vinegar requires that it have a levorotatory reading in the polariscope and when the polarization is dextrorotatory it is considered good evidence of adulteration with commercial "glucose" (which leaves a residue of strongly dextrorotatory dextrin after fermenting), or added sucrose which has escaped fermentation, or gums, used for building up solids. If a too strongly levorotatory reading is obtained, it suggests underfermentation of the apple juice or addition of apple jelly, etc., to the finished vinegar. A dextrorotatory reading becoming levorotatory after inverting is considered proof of added sucrose. The dextrorotatory reading due to the dextrin of commercial "glucose" (or to any unfermented dextrose of the same) is not reversed by the "inverting" process. The natural

dextrorotatory reading of malt vinegar (required by the former standard) is due also to a residue of dextrin coming from the malting of the starch in the grain. The writer (and Dr. Chapman in England) showed that in malt vinegar, the polarization is sometimes found levorotatory, due to certain levorotatory proteins remaining undecomposed. Chapman thought that perhaps even the dextrin of malt vinegar was sometimes fermented out, in an extra-thorough process, leaving mere traces of proteins to account for a slight levorotatory reading in the finished malt vinegar.

The question of what clarifying agent should be used in preparing the cider vinegar sample for the polarization test is very important, as we have pointed out earlier. The official methods of the A. O. A. C. specify that 10 percent of a solution of lead subacetate be added to the cider or apple vinegar to clarify it and weaken the color, before filtering and taking the polariscopic reading, but as said above it is liable to lead to misleading results. A small amount of "Alumina Cream" mixture is preferable.

**Total Ash.** The next test on vinegars, as outlined in the A. O. A. C. official methods of analysis, is the total ash determination. This is the mineral residue left upon evaporating a given quantity of vinegar (as in the test for total solids), and burning the solids thus obtained. Care must be taken that no unburnt particles of carbon remain and the degree of heat used must not make the platinum dish used more than a dull red.

The analytical item thus obtained is a valuable one, especially when further tests upon the total ash are considered. The total ash content of cider and apple vinegars of known purity has been reported as ranging from 0.20 percent to 0.57 percent, averaging about 0.38 percent. Probably the minimum value was a vinegar which had been reduced with water a little. The former Federal standard for cider vinegar required not less than 0.25 percent "apple ash" (total ash) and many State standards have called for the same.

The ash of the apple is made up principally of potassium carbonate (about 68%) and phosphates of potassium and magnesium (about 22%) and the ash of apple juice or vinegar will test practically the same. It is the large proportion of potassium carbonate in "apple ash" which gives it its strongly alkaline character and forms the basis for the Federal standard "alkalinity" requirement. This potassium carbonate does not exist ready-formed in the apple (in fact, could not, as the apple acid would neutralize it), but is a result of the burning process, whereby various potassium salts and other compounds origi-

nally present are converted into potassium carbonate finally, somewhat similar to the well known formation of potassium carbonate when wood is burnt to get wood ashes.

The phosphates resulting from the burning of apple juice or vinegar solids are partly in a soluble form and partly insoluble, the former Federal cider vinegar standard having a legal minimum limit for the proportion of water-soluble phosphate that should be present in the apple or cider vinegar ash. Until somewhat recently there has been a considerable practice of adding phosphates to more or less imitation cider vinegars for the purpose of making them analyze normal in this respect and yet, because various other analytical items were not similarly corrected for, it was frequently a vain precaution, as numerous Federal Notices of Judgment on adulterated vinegars will show.

It is sometimes customary in a vinegar analysis to report also the proportion of the total ash which is soluble in water and, by difference, thus get the proportion of ash insoluble in water. Of course, the greater proportion is soluble, because in addition to the soluble phosphate required in the standard, about 68 percent of the ash is a soluble potassium carbonate, as said above.

**Alkalinity of Soluble Ash, etc.** The next legal analytical requirement is a measure of this potassium carbonate (a mild alkaline substance) and is referred to as the "alkalinity of the soluble ash." It is measured in terms of the number of cubic centimeters of a tenth-normal acid solution required to neutralize the alkalinity (due to potassium carbonate mainly) of the water-soluble ash representing 100 cubic centimeters of the vinegar in question.

The former Federal cider vinegar and apple vinegar standard specified that the "water-soluble ash from 100 cubic centimeters of vinegar" shall require "not less than 30 cubic centimeters of tenth-normal acid solution to neutralize its alkalinity." The reported data on pure products range from 22 cc. tenth-normal acid to as high as 56 cc., the average being about 35 cc.

In the proposed standard for apple juice or must, it is specified that the total ash contain not less than 50 percent potassium carbonate; instead of measuring it in terms of tenth-normal acid required to neutralize it. From the latter item, however, it is a simple matter to calculate how much potassium carbonate is present in the ash.

The former standard for the proportion of soluble phosphate in cider vinegar ash, specifies it in terms of the theoretical acid group in all phosphates, referred to in the standard as "phosphoric acid ( $P_2O_5$ )," and, according to the standard, the "water-soluble ash from

100 cubic centimeters of the vinegar contains not less than 10 milligrams of phosphoric acid ( $P_2O_5$ ).” This can be read also as practically 0.01 percent, and although it may seem a rather insignificant item, yet it has some value in a vinegar analysis, as spirit vinegar (and commercial acetic acid) contains none and malt vinegars much less than vinegars from apples. The soluble ash from malt vinegars also has considerably less alkalinity, while spirit vinegar and acetic acid solutions would show none. Dilution of cider or apple vinegar with water lowers the soluble alkalinity and phosphoric acid proportionately, of course, and on a vinegar properly labeled as being “reduced with water” to minimum legal acid strength (4 percent or 40 “grain”), the analyst corrects for the approximate dilution. The data on samples of known purity show the phosphoric acid in the soluble ash from 100 cubic centimeters of cider vinegar to range from 7 milligrams (0.007 percent) to 40 milligrams (0.040 percent), the average being 17 milligrams (0.017 percent). The phosphoric acid in the water-insoluble ash ranges from 0.004 percent to 0.032 percent, average being 0.012 percent.

**Total Acidity.** Although one of the most important tests from a selling standpoint, the next official test, i.e., total acidity, is not so very important in the legal interpretation of a vinegar analysis.

To be sure, practically every standard, Federal or State, fixes a minimum for acidity in vinegars (usually 4.0 percent, or 40 “grains” in terms of acetic acid), but that requirement complied with, the significance largely ends there. It is only when the acidity is greater than the other data will accommodate, that the addition of a strong spirit vinegar (90 or 100 “grains”) or commercial acetic acid is suspected and further looked for.

The “total acidity” of cider or apple vinegars comprises the so-called “fixed,” or non-volatile, acids and the volatile acetic acid. The total acid in cider and apple vinegars ranges from 3.24 percent to 9.96 percent, in terms of acetic acid, the average being 5.21 percent, in many samples of known purity. The minimum value was, of course, an underfermented vinegar characteristic of farm methods and contained much unfermented sugar due to the acetic fermentation getting started before the alcoholic fermentation was complete. In juice preserved with sodium benzoate, the alcoholic fermentation is stopped or greatly slowed down and the alcohol already formed is converted easily into acetic acid as fast as formed, with the result that the juice becomes unpalatable as a beverage; and as soon as the acetic acid reaches a certain low point, all alcohol production will cease. The

resultant mixture of sour cider and partially made vinegar then becomes practically worthless. This was the principal scientific argument used in the recent test case for permits to make preserved sweet cider, even though the alcohol might exceed the 0.5 percent (by volume) allowed in the prohibition laws.

The total acid of cider or apple vinegar, as said above, is made up of the "fixed" or non-volatile acids and the volatile acetic acid resulting from fermentation of alcohol in the vinegar "stock" or "hard cider." The analytical item "fixed acids" is of some value in judging vinegars and is composed mainly of any residue left of the original apple acid (malic acid) and more or less lactic acid, formed from malic acid and sugars, by fermentation.

In a well made cider or apple vinegar a large part of the malic acid of apple juice is changed into lactic acid during the alcoholic fermentation; and during the acetic fermentation the remaining malic acid is almost completely lost, the fixed acid being then chiefly lactic acid. In the average more or less carefully made cider or apple vinegar there is present both unchanged malic acid and lactic acid with traces (0.01 percent) of succinic acid, formed during the alcoholic fermentation of sugars. In some carefully and completely fermented cider vinegars made by Hartman and Tolman, of the U. S. Bureau of Chemistry, the malic acid ranged from 0.032 percent to 0.045 percent and the lactic acid from 0.23 percent to 0.29 percent. The total fixed acids (usually reported in terms of malic acid) ranged from 0.16 percent to 0.41 percent in about 40 samples of known history or purity. An average value would be about 0.30 percent fixed acids in terms of malic acid.

The fixed acid of grape or wine vinegar would be tartaric acid or acid reacting salts of the same, while other fruit vinegars might show citric acid, characteristic of many fruits.

By subtracting the percent of fixed acid from the total acidity of a vinegar, we get the analytical item "volatile acids." This is, as said above, mainly acetic acid. It is interesting to note, however, that other volatile acids may be present. Even traces of formic acid are formed according to Hartman and Tolman. Other workers have pointed out that formic acid will result from the oxidation of acetylmethylcarbinol, which, we pointed out earlier in this chapter, comprises the analytical item "volatile reducing substance," formed during the acetification of hard cider. These facts should be kept in mind by official inspection chemists, when using the test for formic acid as proof of the addition of commercial acetic acid. Hartman and Tolman also showed

that some of the acetic acid of cider vinegar was present as a neutral non-volatile salt or acetate, in small proportion.

**Volatile Esters.** Although there is no legal requirement for the next item, nor is it specified in the official methods of analysis, yet the determination of "volatile esters" (formerly called "ethers") is rather interesting and valuable as an item showing the bouquet and proper ageing of the vinegar. The esters result from a chemical reaction between the alcohol of the hard cider and various acids, mainly acetic acid. They are measured in terms of the ester ethyl acetate, a very fragrant, volatile substance. Hartman and Tolman reported from 0.79 percent to 0.91 percent volatile esters in a number of well made cider vinegars, made in a rotating generator. The author has seen a sample of very old vinegar, where nearly all the acetic acid had changed to ethyl acetate, due to too much unchanged alcohol being present.

**Color.** The next test in order is that for "color." This is a test which could be advantageously used in the buying and selling of vinegar, as the consumer has the habit of judging a vinegar considerably by its color, in spite of the fact that the quicker and cleaner a vinegar is made the poorer its color from the old standpoint of judgment.

Old methods of selecting, grinding and pressing apples were all conducive towards the final development of a rich brownish-red color in the vinegar, and this color has become the standard looked for in trade circles. The apple is built up of numberless little cells composed of cellular tissue, which in turn is composed of cellulose, lignin and the related hemicelluloses. These tiny cells contain the juice of the apple and, according to how well the cells are disrupted by grinding and how long and thoroughly the pressure is applied, the apple juice is made available for further processing.

The generally accepted explanation of the development of color in ground apples and apple juice (and the ultimate product vinegar also) is that certain of the cells, if not all, contain (in addition to sugar, fruit acid, etc., dissolved in water) a substance known as tannin and an oxidizing ferment, or enzyme, known as oxidase. As soon as the cells are broken by grinding and contents of cells are mixed in the presence of the oxygen of the air, an oxidation of the tannin, by the ferment oxidase, starts with the formation of a brown color. The longer the exposure to air at this stage, the darker the color of the juice will be after pressing and subsequent ageing.

In the older factory and farm procedure, the groundup apple pulp stood for some time before pressing and the pressing itself was a slow



operation, altogether allowing time for considerable degree of color formation. Now, the up-to-date factory prides itself on a quick, continuous process and the resultant apple juice is light in color, sometimes only a faint yellow, and if well protected from air during alcoholic fermentation, the finished vinegar turns out to be a yellow-brown color which, if further diluted with water (while reducing to minimum standard acidity), gives a vinegar very much lighter in color than more carelessly made products.

Attempts have been made to improve the color by adding a small amount of some commercial tannin preparation and agitating the juice to expose it to the air. A high proportion of fruit acid (malic acid) seems to hinder the development of color also. Therefore, sweet apples with a normal tannin content and a moderate standing of the crushed pulp before pressing, are the conditions favorable to the natural development of the rich brown color desired by the trade, in apple juice and vinegar.

The color test consists of measuring the depth of color with a color-comparing instrument called a tintometer. The color is compared with the regular scale of colors used in the brewing industry, but it can be seen, from the preceding statements, that the test has no legal significance, although it might be used to good advantage in the buying and selling of vinegars, where a close uniformity of color was desired.

At this point it is perhaps more appropriate to take up the question of and tests for artificial coloring, than in the A. O. A. C. official testing methods schedule. The chief artificial color used is "caramel," a harmless coloring substance, made by overheating sugars. "Burnt sugar color" is another name for it and various tests have been devised to detect its presence in suspected imitation vinegars, such as spirit vinegars, or dilute acetic acid solutions, appropriately tinted to resemble cider vinegar.

One of the best tests is the color of the vinegar sample, after testing for the "lead acetate precipitate." The natural color is largely precipitated or destroyed, whereas the "caramel" color is little affected. Other colors have been known to be used, certain wood and bark extracts for instance (in which probably the tannin was the most important color-forming ingredient) and also brown coal-tar colors, such as used in artificial chocolate preparations. It is only when the other analytical data show a vinegar to be more or less an imitation product that the color tests become of some legal value as confirmatory evidence.

Liberal minded food chemists are inclined to be very lenient with

an apple juice product that is pure and normal in all respects, except the addition of a trace of "burnt sugar color." However, some laws make a distinct offense of the addition of any artificial color to any vinegar. The addition of color to spirit vinegar, or sugar vinegars, is, of course, for fraudulent purposes.

**Formic Acid.** The next test to be considered, under the schedule of the official testing methods of the A. O. A. C., is the test for formic acid. The presence of more than a certain maximum percentage of matter which will affect the reagent used (mercuric chlorid solution) is considered as proving the presence of formic acid coming from commercial acetic acid, used for increasing acidity or perhaps the only acid present in a wholly imitation vinegar.

A large part of the commercial acetic acid is made by refining the distillate coming from the distillation of wood (hence the obsolete term "wood vinegar") and it unavoidably contains more or less formic acid, which it is impractical commercially to remove. Therefore, an abnormal percentage, in the cider or apple vinegar, of formic acid (or material reacting like formic acid) is considered as very suspicious at least. Probably this is justified in most cases, but it must be remembered that the test does not actually identify the formic acid as such and that other substances in fruit products give the same test, perhaps sometimes in greater proportion than the hitherto reported limits on pure vinegars. These limits, as given by investigators (in the *Journal of Industrial and Engineering Chemistry* for October, 1913), ranged from a "trace" to 0.007 percent in terms of formic acid.

In the February, 1919, issue of the same journal it is stated that the natural formic acid of cider or apple vinegar results from the oxidation of the acetylmethylcarbinol which, we have seen, constitutes the "volatile reducing substance" of fruit vinegars. This item ranges from 0.14 percent to 0.34 percent (in terms of invert sugar) and it is conceivable that the degree of oxidation of the acetylmethylcarbinol might vary considerably according to circumstances.

C. A. Mitchell in his rather insular book on "Vinegar, Its Manufacture and Examination," wherein only his own native malt vinegar receives much attention, makes the following statement: "It is essential that no caramelized (burnt) sugar should be present, for sugar yields appreciable quantities of formic acid when heated to 160° C., at which temperature caramelization begins. Hence as caramel is universally employed for coloring fermentation vinegars . . . no reliance can be placed on the results of the formic acid test if applied to colored vinegars."

As it is the custom of drying "chops" and other apple by-products for the subsequent manufacture of dried apple vinegar, and it is conceivable that sometimes a burning or caramelization of the apple sugars may occur, it seems here is a point to be considered in dried apple vinegar analysis at least.

Moreover, in the *Analyst* for 1911, page 496, formic acid is stated to be a normal constituent of wine vinegar and, as Mitchell adds, "probably also in other kinds of vinegar to which no caramel has been added." The test is evidently one the interpretation of the results of which must be used with caution by official chemists.

**Alcohol Precipitate.** The next test is the "alcohol precipitate" which is intended no doubt to be an index of the presence of dextrin, always present in commercial glucose, which in turn might be used to increase the alcohol yield in hard cider. The alcohol also precipitates pentosans and galactans present. It is an uncertain test, even in a pure vinegar, because when there is considerable unused fruit sugar left in the vinegar and the latter is evaporated to the small volume called for in the test, this sugar will form a gummy, stringy precipitate with the alcohol (characteristic of dextrin) instead of the natural flocculent precipitate it is supposed to form. In absence of quantitative data on the amount of precipitate to be expected from pure cider or apple vinegars, the test is not very conclusive generally and must be used with caution. The polarization and other data serve as a more conclusive evidence of the use of commercial glucose in vinegar manufacture.

**Pentosans.** The next test is another new one, concerning which we have meagre data as to results on pure cider and apple vinegars and the interpretation of which is rather uncertain as yet. It is a well known test in certain vegetable products, cattle feeds particularly, and is called the pentosan determination. The pentosans are products of the group of carbohydrates known as hemicelluloses (intermediate between starch and cellulose), and are derivatives of the cell-wall material of which the innumerable tiny cells of the apple are composed.

As apple pulp is allowed to ferment, the cell-wall material becomes more soluble and a larger proportion of pentosans passes into the juice and subsequent vinegar. It has been thought therefore that the percent of pentosans would prove a valuable index of the condition of the pomace before pressing and serve to detect the old trick of letting first-pressing residue (pomace) stand and ferment (to incipient spoilage) before pressing a second or third time.

In a cider made at the U. S. Bureau of Chemistry in 1905 from

pomace allowed to ferment in large heaps for several weeks, the pentosans tested 0.8 percent, the percent of alcohol precipitate (which would include both pentosans and galactans, resulting from the fermentation) being 1.5 percent; lactic acid to the extent of 0.5 percent was also found and all the usual data differed considerably from a fresh first or second pressing cider.

The proportion of pentosans reported in cider vinegars of known purity and quality ranges from 0.080 to 0.221 percent. In freshly made hard ciders the pentosans range from 0.041 to 0.165 percent. Considerable data seem to indicate that the pentosans nearly double in amount, on the average, as the hard cider undergoes acetification into vinegar. Undoubtedly the test is of value in detecting use of fermented pomace, but more data are desirable for court purposes.

**Miscellaneous Materials.** To conclude the official tests on apple and cider vinegars, there is given a test for "spices and added pungent materials" to be applied to the neutralized sample and a reference to the regular official tests for "preservatives." Good vinegar contains no added preservative, but it is conceivable that some manufacturers might try to convert sweet cider into vinegar and thereby introduce a small percent of sodium benzoate (or benzoic acid), or salicylic acid, or sulfurous acid (from sulfites) into the vinegar. Theoretically this should be indicated on the label, but practically the amount that could be present is very small and would probably not even be tested for, or any official attention paid to it.

### WINE AND MALT VINEGAR

With the exception of a couple of tests for unusual contaminations or adulterations, we have covered the interpretation of a very complete analysis of cider or apple vinegar.

For a wine or malt vinegar, many of the same tests are used and have the same general significance, the main difference being that, for wine or malt vinegar, we find a different range of values for the different analytical items tested for.

The next test in the official testing methods of the A. O. A. C. is one that is used for wine vinegar and corresponds to the item "fixed acid" (malic acid) in apple juice products. The "fixed acid" (non-volatile acid) of wine or wine vinegar would be the natural fruit acid of the grape, viz.: tartaric acid, and its salts (tartrates), especially the "acid salt" known as potassium bitartrate or "cream of tartar."

Following the test for tartaric acid and tartrates comes a test applicable to any vinegar, i.e., a test for mineral acids. It is interesting here to note that in Europe the use of a small proportion of sulfuric acid in apple juice and in various vinegars, has been in the past, and is still to some extent, a commercial practice.

In a recent issue of a well known French scientific journal, Warcollier and Le Moal report a study of the changes taking place in sulfuric acid used to preserve apple juice. They point out that in order to preserve apple juice suitably with sulfuric acid, the fruit must be of good quality and free from molds, as the latter contain oxidizing ferments (enzymes) which alter sugars and glycerol to form compounds which combine with relatively large amounts of sulfuric acid.

In Germany, Meerburg speaks of prepared mustard containing 0.5 percent of sulfuric acid in addition to the vinegar used and in earlier days the British Government specifically allowed sulfuric acid to be added to vinegar (presumably malt vinegar) in the proportion of 0.1 percent by weight. Nowadays the practice is practically extinct in England and in this country the addition of any mineral acid to vinegars for any purpose is officially prohibited.

The test applied is usually merely a qualitative one, depending upon color changes with certain "indicators" (dyes) when any mineral acid is present. Of course, if necessary the test can be made quantitative.

The next official test is for metallic contamination which might be present in carelessly handled vinegars. Certain metallic contaminations would be a quite serious matter; thus if any vinegar came in contact with lead piping, etc., there would be formed the very poisonous acetate of lead, sometimes called "sugar of lead." Zinc would form objectionable salts with acetic acid and copper (or brass) particularly would give poisonous salts having a brilliant, blue-green color. Verdigris is a variety of copper acetate.

The action of acetic acid on iron would be to form an iron acetate, which, uniting with any tannin present, forms practically an "ink," which in sufficient quantity would turn apple cider or vinegar nearly black in color.

The next test we come to has already been referred to under the "alcohol precipitate" test, and is listed as a "qualitative test" for dextrin. As the "alcohol precipitate" may be composed of pentosans and galactans under certain circumstances, in order to make it distinctive as a test for dextrin, the analyst is directed to further test the precipitate by means of a polariscope and by the characteristic

color given with iodine solution. The dextrins give a strong dextro-rotatory reading in the polariscope and, in general, a study of the data on the polarization of the cider or apple vinegar will furnish good evidence of the presence of dextrin, coming usually from use of commercial "glucose" of which it is a regular ingredient.

Malt vinegars will have dextrin present as a natural constituent, coming from the malting of the cereal used in preparing the wort and subsequent gyle. In the former standard for malt vinegar, it is required that the polarization be dextrorotatory and this is usually the case, due to the aforementioned presence of dextrin. The polarization of malt vinegar may, however, be sometimes levorotatory even as high as  $-1.5^{\circ}$  Ventzke. This was shown by the author in 1911, and by Chapman in England (1912), to be due to the presence of undecomposed proteins, which are levorotatory.

Possibly the underfermentation of the proteins was due to the use of the pure sugar-forming ferment of malt (diastase), instead of the whole malt, which can convert proteins into peptones, amides, etc. Chapman considered it due, however, to an extra-thorough fermentation of the carbohydrates, in which all of the dextrin was used up, allowing a small residue of proteins to give a levorotatory polarization.

## Chapter IV.

### The Legal Chemistry of Some Condimental Sauces.

#### TOMATO CATSUP \*

Among the condimental sauces and relishes containing vinegar as an important ingredient, tomato catsup is perhaps the most generally used product of that nature in this country. In addition to certain lego-chemical phases of the vinegar content, tomato catsup also involves the consideration of a well-known fruit (the tomato) and here again some more food inspection chemistry is involved.

A few catsup manufacturers use fruit vinegars, but by far the greater proportion of tomato catsup is made with spirit vinegar, preferably "grain vinegar." There is, however, considerable illegal use of commercial acetic acid solutions in cheaper grades of catsup, in place of vinegar; and in a number of the better grades more or less commercial acetic acid is introduced in the form of an "acetic acid extract" of the various spices used to modify the flavor of the catsup.

This last practice is considerably less reprehensible, from a legal standpoint, than the complete substitution of vinegar by commercial acetic acid solution, but, strictly speaking, it should be stated on the label in some form. It has been found that the spices can be advantageously extracted of their flavoring constituents (mainly essential oils) by soaking in fairly strong acetic acid and a relatively small amount of this acetic acid extract of the mixed spices can be added to the catsup after the cooking process is ended, thereby avoiding the great loss of flavoring material (essential oils, etc.), which results when ground spices are cooked and the oils virtually "distilled off with steam."

The bulk of the acetic acidity of a catsup should come from vinegar, however, and the test for formic acid (as proof of the appreciable use of commercial acetic acid) is so delicate that any substitution is risky, unless admitted on the label.

\* Originally published in *The American Vinegar Industry and Fruit Products Journal*, June, 1923, and *The Spice Mill*, Sept., 1924, *et seq.*

The Federal food standard definition of tomato catsup is as follows: "Catchup (ketchup, catsup) is the clean, sound product made from properly prepared pulp of clean, sound, fresh ripe tomatoes, with spices and with or without sugar and vinegar; mushroom catchup, walnut catchup, etc., are catchups made as above described, and conform in name to the substances used in their preparation."

In catsup, vinegar is not used in preservative proportion, but is used rather as a condiment, to furnish acidity. Some of the acidity of a tomato catsup comes from the natural fruit acid of the tomato, i.e., citric acid, and a little acidity (0.2 to 0.3 percent) results from the lactic acid, formed by bacteria, from fruit sugars in the tomato pulp. As tomato products ferment or spoil, the proportion of citric acid decreases (molds seem to remove the citric acid rapidly) and the proportion of lactic acid increases and ultimately the disagreeable volatile butyric acid is formed in detectable quantity.

A good catsup is characterized by fairly high citric acid content (0.5 to 0.8 percent) and slight lactic acid content. The fresh, sound tomato or tomato pulp, contains no volatile acid (citric and lactic acids are non-volatile acids) and in unspiced tomato catsup the volatile acidity is due to acetic acid from vinegar and ranges generally from 0.5 to 1.5 percent (or 5 "grains" to 15 "grains"). Of course, in the cooking of tomato catsup, considerable volatile acetic acid is lost.

Tomatoes vary considerably in composition, but are, at the best, mainly water, the total solids seldom exceeding 6 percent and averaging nearer to 5 percent. These solids are composed of, on the average, about 2.5 percent reducing sugars, about 0.5 percent citric acid, 0.8 percent "protein" ( $N \times 6.25$ ), 0.5 percent fiber, 0.2 percent fatty oil and about 0.5 percent ash. In the commercial manufacture of tomato catsup, the skins, seeds and more solid parts of the core are screened out, leaving what is known as "cyclone juice," and this juice is then concentrated by evaporation, to a specific gravity of 1.035 (68° F.), constituting then what is known as "tomato pulp." This "pulp" is the actual basis of the catsup and at the above specific gravity will contain about 8.5 percent total solids and weigh somewhat over 8 pounds, 10 ounces to the gallon when cold.

The skin constitutes about 10 percent of the tomato and seeds about 5 percent. In the canning of tomatoes, the tops are sliced off and the skin and core so roughly removed that considerable pulpy, fleshy material of the tomato adheres. It is customary to use these "trimmings" (cores, skin, etc.) to make a slightly lower grade of



"pulp," and if the whole fruit is sound and ripe, there is no reason why a given batch of tomatoes should not yield both the canned product and a good grade of "pulp" for making catsup.

For many years, however, some very careless, aye filthy, methods prevailed in the canning factories, the sorted-out moldy and (sometimes) half-rotten tomatoes being added to the "trimmings" which, together with any green or malformed tomatoes delivered at the factory, constituted the raw material for making "pulp" for catsup manufacture. This has been largely done away with by Federal inspections of canning factories and many prosecutions and condemnations of shipments for showing an excess of mold or yeasts, under the microscope.

The pulp and subsequent catsup made from "trimmings" analyze slightly different from the products made from whole tomatoes, when the data are calculated to a dry, sugar-free and salt-free basis; and from Table 38 showing analyses of a rather watery grade of tomato we have calculated the results to a dry (water-free) basis, as a basis to compare the pulp and catsup with, later on.

Table 38. Analyses of Tomatoes.

	<i>Whole Fruit</i>	<i>Cyclone Juice</i>	<i>Skins</i>	<i>Seeds</i>
	Percent			
Total solids .....	4.37	3.62	6.46	12.55
Insoluble solids .....	1.44	0.64	3.62	10.30
Soluble solids .....	2.93	2.98	2.84	2.25
Sugars .....	2.37	2.25	3.15	2.91
Sugar-free solids .....	2.00	1.37	3.31	9.64
Crude fiber .....	0.46	0.22	1.75	1.93
Ash .....	0.42	0.41	0.48	0.44
Fatty oil .....	0.27	0.09	0.11	3.38
"Protein" .....	0.85	0.65	0.97	3.89
Acidity (as citric acid) .....	0.50	0.35		

Table 38 calculated to a dry basis gives the results and ratios shown in Table 39.

Table 39. Analyses of Tomatoes (water-free basis).

	<i>Whole Fruit</i>	<i>Cyclone Juice</i>	<i>Skins</i>	<i>Seeds</i>
	Percent			
Insoluble solids .....	32.95	17.68	56.04	82.07
Soluble solids .....	67.05	82.32	43.96	17.93
Sugars .....	54.23	62.14	48.76	23.18
Sugar-free solids .....	45.77	37.86	51.24	76.82
Crude fiber .....	10.53	6.08	27.09	15.38
Ash .....	9.61	11.33	7.43	3.51
Fatty oil .....	6.18	2.49	1.70	26.93
"Protein" .....	19.45	17.96	15.02	31.00
Insol. solids in sugar-free solids ....	71.9	46.7	109.3	....
Fibre in sugar-free solids .....	23.0	16.0	52.9	....
Ash in sugar-free solids .....	20.9	29.9	14.5	....

The data of most interest in the calculation of tomato constituents to a dry basis are the last three ratios, for by calculating the tomato catsup to a similar dry, salt-free and sugar-free basis it will be seen that the catsups of known purity have very similar ratios to those given above for cyclone juice. The above three ratios for the whole fruit are, of course, rendered useless by the inclusion of the seeds, while as concerns skins, one can not expect to find the ratio of fiber to sugar-free solids duplicated in so-called "core and skin" (trimmings) pulp catsups, because the fibrous true skin is also largely kept out of catsup.

The pulp, which is the basic material of tomato catsup, is made, as said above, by salting and concentrating the cyclone juice (from whole tomatoes or from trimmings) approximately to the standard specific gravity (1.035) or, roughly, to about double the consistency of the cyclone juice. Pulp of this grade will analyze about as shown in Table 40.

Table 40. Tomato Pulp.

	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Specific gravity (68° F.) .....	1.025	1.046	1.035
		Percent	
Total solids .....	6.67	10.24	8.50
Salt (added) .....	0.00	1.30	0.50
Salt-free solids .....	5.37	10.09	8.00
Insoluble solids .....	0.81	1.63	1.25
Reducing sugars .....	1.50	5.66	4.50
Acidity (as citric acid) .....	0.38	0.80	0.70

This tomato pulp is also the basis for the manufacture of purees and tomato pastes of different consistency, some of which are canned and others preserved by an excess of salt.

During the cooking of the pulp with the various ingredients considered necessary by different catsup manufacturers, such as sugar, salt, spices, garlic, onions, vinegar, etc., to form catsup, there is a further concentration of the original cyclone juice so that a finished catsup is from three to four times as concentrated as the original juice or about double the concentration of the tomato pulp.

The following recalculated analyses of ten catsups, known to be whole tomato pulp products, and five known or judged to be made mainly from trimmings, show particularly the value of the ratio between insoluble solids and the "sugar-free and salt-free solids." The reversal of the ratio of "salt-free ash" to "sugar-free and salt-free solids," the author attributes to the dirtiness of the "trimmings" as often sold.



The following data suggest standard limits for a good catsup, viz.: Insoluble solids not less than thirty (30) percent nor more than sixty (60) percent of the sugar-free, salt-free solids; crude fiber not more than sixteen (16) percent of sugar-free, salt-free solids; salt-free ash not more than thirty (30) percent of sugar-free, salt-free solids; and the sugar-free, salt-free solids not less than four (4) percent.

The last requirement would cause the rejection of two of the catsups of known purity, but as one sells for a very high rate per pound, the manufacturer can afford to sell a little more tomato with less sugar if necessary. This brand, by the way, is just on the borderline of the above proposed standard throughout.

It must be remembered that from 0.5 to 0.8 percent of the acidity in a catsup made from sound fruit will be due to the fruit citric acid of the tomato, hence it will appear that certain brands contain very little vinegar or that the volatile acetic acid of the vinegar has been largely lost by cooking.

Various faulty proposed standards for tomato catsup have been published, usually calling for a certain proportion of "total solids" or "soluble solids." These disregard entirely the fact that sugar is used by different catsup manufacturers, in widely varying proportions, so that if one manufacturer is making what might be called a "tomato jam" containing 25 percent sugar, and another was selling much more tomato pulp and only a very little sugar, the former's product would comply with the standard proposed, while the latter's would not!

Obviously, the only fair basis of judgment is to calculate the data to a dry, sugar-free, salt-free basis (see analytical item "sugar-free, salt-free solids") and then make comparisons.

We have mentioned the custom of the Federal (and some State) officials in judging the legal cleanliness of tomato catsups, etc., from a microscopical estimation of molds, yeasts and bacteria. An excess of yeasts indicates usually that fermentation of the tomato "pulp," or finished tomato catsup or paste, has taken place, but it must not be overlooked that this constitutes an old, well known, though somewhat foolish, method of preparing catsup and that certain kinds of tomato paste are purposely allowed to ferment. Bacteria, too, would be excessive in such products.

In tomato catsup inspection it has always seemed to the author that the interpretation of molds as evidence of a certain percentage of decomposition (rot) in the original tomatoes should be substantiated

by chemical data. Some molds cause rot and rotten parts of a tomato are frequently infested with molds, but because some factory experiments showed an approximate relationship between the mold count and the percent of rot, it does not follow that all mold indicates rot, especially in those food inspection cases where nothing is known of the history and condition of the original tomatoes.

When a tomato cracks (especially small radiating cracks at the stem end) from too rapid growth during wet weather, the cracks quickly become filled with a delicate white mold, although the flesh beneath is firm and undecomposed. Also the black or brown rot may be visible as but a small speck on the skin (which would naturally not lead to rejection) although a deep-seated core of growth might exist and give a high mold count.

A high mold count should simply be a sign indicating the desirability of a chemical analysis to estimate an appreciable decomposition (if any); and to base a prosecution on the mold count alone and condemn big shipments thus, as has been done hundreds of times because canners would rather not elect to contest Government officials, seems utterly unscientific and unfair.

It is not as if nothing were known of the chemical changes taking place during the spoilage of tomatoes. On the contrary, several of the U. S. Bureau of Chemistry's best men have carefully studied the chemical changes taking place during the spoilage of tomatoes and have published an official "Circular" (No. 78) on the "Changes Taking Place During the Spoilage of Tomato Products."

It was shown clearly in the case of rot caused by mold, that the citric acid of the tomato was rapidly decreased and, by associated bacterial action, lactic acid and volatile acids (butyric acid) were formed. The butyric acid would be lost in cooking operations but the non-volatile lactic acid would remain. Thus on sound and spoiled raw tomatoes (both from same batch) the data of Table 42 were determined.

Table 42. Change of Composition of Tomatoes on Rotting.

	Sound Tomatoes	Spoiled Tomatoes	
		After 10 Days	After 2 Weeks
		Percent	
Total solids .....	5.80	3.66	...
Reducing sugars .....	3.30	None	...
Citric acid .....	0.59	...	None
Lactic acid .....	None	0.48	0.37
Volatile acids (as butyric acid) .....	None	0.12	0.46
Free ammonia .....	0.040	0.056	0.068

Four samples of tomato pulp which were known to be made from inferior raw material or had undergone fermentation, showed little or no citric acid left and lactic acid ranging from 0.42 to 0.75 percent. Three others known to be good quality showed citric acid to range from 0.38 to 0.52 percent, with only a slight lactic acid content, ranging from 0.07 to 0.20 percent. Three samples of pulp were inoculated with mold and allowed to spoil. The citric acid content was greatly lowered (practically none left in two cases) and lactic acid was formed, as high as 0.27 percent in one case.

These experiments plainly show that any appreciable spoilage, due to molds mainly, can be detected by a chemical estimation of the citric acid (which would not be affected by the cooking and spicing of catsup making) and that bacterial spoilage can be detected by the formation of lactic acid in excessive quantity and formation of volatile acids and free ammonia.

In U. S. Bureau of Chemistry Bulletin 152 (p. 121) McGee, reporting as associate referee in the "Association of Official Agricultural Chemists," made two samples of catsup by exactly the same recipe, one from clean, sound tomatoes and the other from same tomatoes which had been allowed to stand until each had started to decay and were infested with mold. These two catsups were then analyzed by three different chemists (the agreement between the different analysts being generally good) with average results shown in Table 43.

Table 43. Analyses of Catsups Made from Sound and Moldy Tomatoes.

	Tomato Catsup (sound fruit)	Tomato Catsup (moldy decayed fruit)	Approximate Loss
	Percent		
Total solids .....	23.50	19.30	18
Insoluble solids .....	2.34	1.84	18
Soluble solids .....	21.10	17.40	18
Total sugars (after inversion) .....	15.20	12.40	18
Citric acid .....	0.52	0.38	22
Lactic acid .....	0.30	0.59	100 gain
Nitrogen .....	0.34	0.24	30
Pectin .....	1.17	0.87	30
Protein (N $\times$ 6.25) .....	2.14	1.53	30

The total solids, soluble solids and sugars depend upon the proportion of sugar used in making the catsup, but the other items are independent of this and would not be appreciably affected by cooking processes. The data as a whole show that profound changes take place, capable of measurement by chemical methods. The lowering of the insoluble solids show destruction of the cell-wall tissue of the

tomato, by mold growth; the citric acid has been largely decreased by the same cause and the lactic acid doubled in quantity by the accompanying bacterial growth. The nitrogenous products ("protein") have been decomposed and nitrogen lost (as ammonia and amines) and even the pectin is affected.

It seems very conclusive, therefore, that really excessive mold growth, causing appreciable rot and spoilage of tomatoes, is detectable by exact chemical methods, and it is the author's opinion that unless chemical data confirm the microscopic "counts," tomato products should not be destroyed off-hand in wholesale quantities as has been and is being done. If a tomato pulp, catsup or paste analyzes chemically normal throughout, it is entitled to all the doubts accompanying the microscopical counting methods for molds and bacteria.

#### PREPARED MUSTARD

This product is one of the most acceptable and used of the various condimental sauces containing vinegar and, in this country, as in the case of tomato catsup, the vinegar generally used in making it is spirit vinegar. In prepared mustard the vinegar is used for both acid taste and preservative qualities, but much of its preservative value depends upon the co-operating effect of the volatile oil of mustard; in fact, a proportion of vinegar acidity that will serve as a preservative in a genuine mustard paste frequently fails in a paste made from mustard-seed substitutes or combinations of true mustard seeds which yield little or no volatile oil of mustard. Thus white mustard (*Sinapis alba*) alone yields very little volatile oil upon macerating with water or vinegar, and from all standpoints it has been found desirable to mix white mustard with black, brown or Oriental yellow mustards in order to get the flavor and preservative effects of the volatile mustard oils yielded by those varieties.

According to the Federal food standards (Circular 136, Office of the Secretary, United States Department of Agriculture), "mustard seed is the seed of *Sinapis alba*, L. (white mustard), *Brassica nigra* L. Koch (black mustard), *Brassica juncea* Hook f. et Th., or varieties or closely related species of the types of *Brassica nigra* and *Brassica juncea*." "*Sinapis alba* (white mustard) contains no appreciable amount of volatile oil. It contains not more than five percent (5%) of total ash, nor more than one and five-tenths percent (1.5%) of ash insoluble in hydrochloric acid."

"*Brassica nigra* (black mustard) and *Brassica juncea* yield (at

least) six-tenths percent (0.6%) of volatile mustard oil (calculated as allyl isothiocyanate and determined by the method given in Service and Regulatory Announcements, Chemistry 20). The varieties and species closely related to the types of *Brassica nigra* and *Brassica juncea* yield not less than six-tenths percent (0.6%) of volatile mustard oil, similar in character and composition to the volatile oils yielded by *Brassica nigra* and *Brassica juncea*. These mustard seeds contain not more than five percent (5%) of total ash, nor more than one and five-tenths percent (1.5%) of ash insoluble in hydrochloric acid."

The Service and Regulatory Announcement mentioned above also specifies that whole mustard seed must not contain more than 5 percent of foreign seed or other foreign matter and specifically mentions *Brassica cernua*, Thumb. (so-called Chinese or Japanese mustard seed) as a variety or species "closely related to the types of *Brassica nigra* and *Brassica juncea*." This Chinese or Japanese mustard seed is bright yellow in color when ripe, but is usually sold with a large proportion of greenish colored unripe seeds, together with some brown mustard seeds of related species or varieties. Unlike the English, California, German, or Roumanian, white or yellow mustards (*Sinapis alba*, L.) which yield but traces of volatile oil, this Chinese or Japanese mustard (*Brassica cernua*, Thumb.) yields only a little less volatile mustard oil than do the black (*Brassica nigra*) and brown (*Brassica juncea*) varieties and it is recognized as the equivalent of the latter in the Japanese Pharmacopoeia.

A great deal of this Chinese or Japanese yellow mustard seed, having approximately the same condimental value as black or brown mustards, is being imported and sold cheaply and, when ripe and free from excess of weed-seeds which cause fermentation, it can replace a considerable proportion of the customary black or brown seeds, this privilege being specifically allowed in Service and Regulatory Announcement, Chemistry 14.

In contradistinction to this yellow mustard having the condimental volatile oil yielding value of black mustard, we have also a black wild mustard seed which closely resembles *Sinapis alba* in composition, yielding but a slight proportion of volatile oil. This is the wild mustard seed known as charlock (*Sinapis arvensis*, L.), which for some reason, probably because it can be cheaply bought as a by-product from the cleaning of wheat and therefore is not cultivated, is not allowed (according to Federal Food Inspection Decision 137) to be used as a mustard seed. The Decision reads: "It is the



opinion of the board that when charlock is substituted in part for mustard the label should clearly indicate the fact. A condiment prepared from mustard or mustard flour and charlock with salt, spices, and vinegar is not "Prepared Mustard," but, provided a greater quantity of mustard than charlock is used, it should be called "Prepared Mustard and Charlock."

In two test cases, where the United States Department of Agriculture has tried to prosecute under the above arbitrary dictum, the Government has been decisively beaten in court. In the first case (see Notice of Judgment 1552), the author was expert for the defense against a half dozen Government chemists and botanists and in the second case (see Notice of Judgment 4811), the Federal Judge (Anderson) held that there could be a "pure wild mustard," that charlock was wild mustard, and that there was no misbranding because wild mustard had been sold as "pure mustard." However, in spite of these defeats, Food Inspection Decision 137 has not been rescinded and in general the trade are careful not to use mustard seeds containing more than traces of charlock.

Among the really serious adulterations of mustard seeds, the various rape-seeds should be mentioned, on account of the frequently close similarities between the related species and because the use of a rape-seed, instead of a volatile mustard oil yielding seed, means disagreeable flavor in the "prepared mustard" and an absence of volatile oil of mustard to assist the vinegar in preventing fermentations.

About ten years ago, big shipments of a Chinese yellow rape-seed (Colza or *Brassica campestris*, variety Sarson) were imported as rape-seed and then resold as a "yellow mustard," which it somewhat resembled. This caused the spoilage of vast quantities of "prepared mustard" until the fraud was detected by the author. Later the U. S. Department of Agriculture seized several big shipments and the author served as expert for the Government in the test case which ended the fraudulent scheme. The rape-seed in question (Colza or Sarson) yielded about 0.4 percent of a volatile oil smelling like radish, but having little or no preservative value.

The odor of a pure prepared mustard is a very characteristic, pleasing one and is due mainly to the volatile oil of mustard, as is also due much of the flavor. The "bite" or stinging taste is due to volatile mustard oil and a non-volatile sinalbin sulfocyanide yielded by ordinary white or yellow mustard (*Sinapis alba*) upon macerating with water, or vinegar, or both.

The mustard seeds which yield the volatile oil of mustard are distinguished from those which yield little or none (*Sinapis alba* or white mustard and *Sinapis arvensis* or charlock) by being reticulated, i.e., the surface of the seed showing a fine network. Two of the brown rapes show distinctly reticulated surfaces, i.e., Palai Rape (*Brassica rugosa*, Prain) and Tori or Brown Indian Rape (*Brassica Napus*, L. var. *dichotoma*, Prain), but neither of them yield the legally required amounts of a volatile oil, much less a volatile mustard oil. The following data (Table 44) show the range in composition in various mustard seeds and in brown and yellow rape-seeds. The latter show considerably more fatty oil and less "protein" and "reducing substances," than do the mustard seeds.

Table 44. Analyses of Mustard Seeds<sup>1</sup> and Rape Seeds

	White Mustard ( <i>Sinapis alba</i> )	Charlock ( <i>Sinapis arvensis</i> )	Black or Brown Mustard ( <i>B. nigra</i> or <i>junceae</i> )
	Percent		
Volatile oil .....	0.04 to 0.1	0.1 to 0.22	0.65 to 1.38
Fatty oil .....	22.6 to 32.3	21.4 to 30.1	26.0 to 39.8
Crude fiber .....	4.8 to 6.7	7.1 to 9.3	4.2 to 8.0
Nitrogen .....	3.9 to 5.4	4.0 to 5.2	3.5 to 4.8
"Protein" (N × 6.25) .....	24.3 to 33.7	27.4 to 28.1	21.9 to 30.0
Reducing substances* .....	8.7 to 13.7	9.1 to 12.9	7.8 to 14.0
Total ash .....	3.6 to 5.5	4.0 to 4.9	3.7 to 8.9
Phosphorus as P <sub>2</sub> O <sub>5</sub> .....	1.5 to 2.6	.....	1.7 to 2.5
Iodine No. of fatty oil .....	93. to 103.5	119. to 121.	100. to 122.
Sapon. No. of fatty oil .....	170. to 175.	181. to 183.	173. to 179.

	Chinese Mustard ( <i>Brassica cernua</i> )	Brown Rape ( <i>B. Napus</i> , etc.)	Yellow Rape ( <i>Colza</i> or <i>Sarson</i> ) ( <i>B. campestris</i> )
	Percent		
Volatile oil .....	0.7 to 1.0	0.3 to 0.46	0.42 to 0.48
Fatty oil .....	33.7 to 43.9	41.8 to 47.0	40.0 to 45.8
Crude fiber .....	3.7 to 4.5	4.1 to 6.2	3.9 to 4.2
Nitrogen .....	3.9 to 4.4	.....	.....
"Protein" (N × 6.25) .....	24.3 to 27.5	22.7 to 24.3	22.4 to 24.8
Reducing substances* .....	12.5 to 13.1	11.0 to 11.6	11.3 to 11.7
Total ash .....	3.9 to 8.4	4.4 to 5.4	5.5 to 6.5
Phosphorus as P <sub>2</sub> O <sub>5</sub> .....	1.3 to 2.0	.....	.....
Iodine No. of fatty oil .....	108. to 117.	94.0 to 105.0	96.5 to 100.
Sapon. No. of fatty oil .....	.....	169. to 177.	169. to 174.

\* After inversion and calculated as starch (no true starch in mustard seeds). Well dried mustard seeds contain about 7 percent moisture.

The Federal standard for "ground mustard seed, mustard meal" defines it as "unbolted, ground mustard seed," and "conforms to the standards for mustard seed." "Mustard flour, mustard" is defined

<sup>1</sup> See *J. Assoc. Official Agri. Chem.*, Aug., 1923, p. 72-5, for data on different varieties of brown, yellow and Oriental seeds. Also see Chapter VII on "The Legal Chemistry of Spices," under Mustard.

as "the powder made from mustard seed with the hulls largely removed and with or without the removal of a portion of the fixed (fatty) oil" and "contains not more than one and five-tenths percent (1.5%) of starch, nor more than six percent (6%) total ash." The limit of 1.5 percent for starch is for the purpose of accommodating any traces of starch-containing weed-seeds that may be present (within the 5 percent limit of foreign matter); but it must be remembered that pure mustard itself contains no starch at all. The hulls, which are removed in the preparation of "mustard flour," are the commonest adulterant of prepared mustard, and the limit for crude fiber in the Federal Standard for prepared mustard is for the purpose of detecting any excess of hulls, over and above those coming from grinding the whole seed, when making prepared mustard. The microscope will quickly demonstrate the presence of any uncooked starch in mustard. Table 45 shows the analytical limits found in twenty-three samples of commercial ground mustard, examined in the Connecticut and Massachusetts food inspection departments.

Table 45. Analyses of Commercial Ground Mustards and Flours.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	5.09	9.50
Non-volatile ether extract (fatty oil) .....	12.65	38.47
Alcohol extract .....	19.22	25.31
Nitrogen .....	5.70	7.44
"Protein" (N x 6.25) .....	35.63	46.50
Crude fiber .....	1.58	4.87
Starch (diastase method) .....	0.00	2.08
Total ash (mineral residue) .....	4.36	7.35
Ash insoluble in acid .....	0.08	0.50

The Federal standard for prepared mustard calculates the crude fiber and other analytical limits to a water-free, fat-free and salt-free basis and in the Massachusetts data included above (three samples of brown mustard seed "flour" and two samples of yellow mustard seed "flour") the values of Table 46 were obtained.

Table 46. Analyses of Mustard Flours (on dry, fat-free basis).

	<i>Brown Mustards</i>		<i>Yellow Mustards</i>	
	<i>Minimum</i>	<i>Maximum</i>	<i>Minimum</i>	<i>Maximum</i>
	Percent			
Alcohol Extract .....	26.64	32.88	29.93	30.13
Nitrogen .....	8.27	9.61	9.00	9.20
Crude fiber .....	3.15	4.26	2.31	3.20
Starch (diastase method) .....	6.75	15.43	7.54	8.34

As prepared mustard is nearly always made by grinding the whole seed, it is of interest to see how the various constituents of whole mustard seeds figure out when calculated to a dry, fat-free basis (Table 47).

Table 47. Analyses of Mustard Seeds (on dry, fat-free basis).

	<i>Brown Mustards (17)</i>		<i>Yellow Mustards (22)</i>	
	<i>Minimum</i>	<i>Maximum</i>	<i>Minimum</i>	<i>Maximum</i>
	Percent			
Alcohol Extract .....	24.33	24.54	23.69	26.85
Nitrogen .....	6.42	8.00	6.00	8.35
Crude fiber .....	7.24	11.00	7.34	11.00
Carbohydrates* (as starch) .....	11.94	13.03	12.74	15.91
Phosphorus as $P_2O_5$ .....	2.92	4.40	2.30	4.13
Calcium (as $CaO$ ) .....	0.85	1.73	0.73	1.30
Magnesium (as $MgO$ ) .....	0.85	1.33	0.61	0.98
Ratio Nitrogen to Crude Fiber .....	0.56	1.00	0.59	1.00
Ratio $P_2O_5$ to Crude Fiber .....	0.28	0.42	0.28	0.46
Ratio $CaO$ to $MgO$ .....	0.84	1.71	0.96	1.69

Oriental (Chinese) seed shows about same range of values as brown mustards, except crude fiber which ranges from 7.2 to 8.3 percent.

\* Acid method.

It will be seen that the highest value we have for crude fiber (calculated to a dry, fat-free basis) in either mustard flour, or ground whole mustard seeds, is 11 percent as compared with the 12 percent limit allowed in the Federal standard for prepared mustard. Moreover this value was obtained on a single yellow mustard (a Dutch seed) and on a single brown seed from Chile; and a yellow (or white) mustard seed alone would never be used for making a prepared mustard, as the product would be deficient in volatile mustard oil, upon which depends the odor, preservative value and, to some extent, the flavor. None of the brown mustard seeds showed over 11 percent crude fiber, when calculated to a dry, fat-free basis, but there are brown seeds containing as high as 8 percent fiber, which, when calculated to a dry, fat-free basis, would approach fairly near to or even exceed the 12 percent crude-fiber limit of the Federal standard for prepared mustard.

Mustard hulls themselves, containing from 10.77 percent to 25.18 percent crude fiber, would figure out from 14.10 percent to 29.20 percent (average 21.11%) crude fiber, when calculated to a dry, fat-free basis (see below).

The new Federal standard for Prepared Mustard provides for the use of "Mustard Cake," which is legally defined as "ground mustard seed, mustard meal (see above) from which a portion of the fixed (fatty) oil has been removed." In full the Federal standard

for "Prepared Mustard" defines it as "a paste composed of a mixture of ground mustard seed and/or mustard flour and/or mustard cake, with salt, a vinegar, and with or without sugar (sucrose), spices, or other condiments. In the fat-, salt-, and sugar-free solids it contains not more than twenty-four percent (24%) of carbohydrates, not more than twelve percent (12%) of crude fiber, nor less than five and six-tenths (5.6%) of nitrogen, the carbohydrates being calculated as starch."

As to the composition of mustard hulls, or mustard-bran, it is desirable to study it by the same chemical data as determined on the whole seed (or meal) and "flour," and especially on a dry, fat-free basis, as it is only by such comparison that small additions of mustard-bran to prepared mustard can be detected. Some quite extensive analyses of nineteen commercial mustard brans have recently been reported by Hertwig (see *J. Assoc. Official Agri. Chem.*, Nov. 1923), supplementing the extensive analyses (43 in all) of yellow, brown and Oriental (China and Japan) mustard seeds in the August, 1923, issue of the same journal (Table 47). When these are calculated to a water- and fat-free basis, as in the case of the mustard flours and particularly the mustard seeds (see above), we have the same basis as the standard for a prepared mustard and also a means for detecting added bran.

Table 48. Analyses of Commercial Mustard-Brans.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Original Bran		
Moisture .....	6.82	11.08
Fatty oil .....	5.86	17.89
Nitrogen .....	2.28	4.52
Crude fiber .....	10.77	25.18
Total ash .....	4.29	5.68
Acid insoluble ash .....	0.01	0.61
Phosphorus as $P_2O_5$ .....	0.34	1.85
Calcium (as CaO) .....	0.64	1.61
Magnesium (as MgO) .....	0.22	0.60
Dry, Fat-Free Basis		
Nitrogen .....	2.70	5.92
Crude fiber .....	14.10	29.20
Phosphorus (as $P_2O_5$ ) .....	0.40	2.42
Calcium (as CaO) .....	0.86	1.91
Magnesium (as MgO) .....	0.27	0.79
Ratio Nitrogen to crude fiber .....	0.09	0.42
Ratio $P_2O_5$ to crude fiber .....	0.01	0.17
Ratio CaO to MgO .....	1.70	7.20

By comparing the amounts of  $P_2O_5$ , CaO and MgO, and especially the three ratios, with similar items as given under the mustard seeds

(on dry, fat-free basis) we find differences so great that the presence of small proportions of added bran (that would not be revealed by the crude fiber alone) becomes possible of detection.

A supplementary Service and Regulatory Announcement (Chemistry 28) specifically says that "prepared mustard," "mustard dressing," etc., "are deemed adulterated and misbranded if they contain any added mustard-bran." If the added bran (hulls) does not predominate, the product can be labeled "prepared mustard and mustard-bran," or "mustard and mustard-bran dressing" or equivalent expressions. "The name 'prepared mustard' or a synonym followed by a list of ingredients including mustard-bran is not regarded as proper." Where the mustard product present is essentially mustard-bran (hulls) the article is regarded as an "imitation prepared mustard and should be labeled as such, with a declaration of the presence of mustard-bran and such other ingredients as may be responsible for imparting to the article its characteristics as an imitation."

An early Service and Regulatory Announcement (Chemistry 5) says the "addition of turmeric to prepared mustard is not prohibited, provided the coloring added by means of turmeric does not conceal damage or inferiority. The presence of turmeric should in all cases be declared upon the label." The previous Federal standard for pre-prepared mustard ruled out turmeric as a spice which would "simulate the color of yellow ground mustard." This was a direct contradiction to the above Service and Regulatory Announcement. The new Federal standard (Food Inspection Decision 192) says nothing that can be construed as prohibiting turmeric.

Turmeric is a well known spice and Dr. A. L. Winton, who analyzed the prepared mustards upon which the Federal standard is based and who largely formulated the Federal standard itself, says, "Turmeric is not only a color, but also a spice, and its use is therefore unquestionably permissible." The stand taken in the old Federal prepared mustard standard was therefore rather arbitrary, to put it mildly, and in a test case (Notice of Judgment 1552), in which the author appeared as expert for the defense, some ten years ago, the six Government experts were decisively beaten and the Federal Judge (Holt) ordered an acquittal, holding that turmeric was a spice and as such was a permissible ingredient of prepared mustard, whether stated on the label or not. Most manufacturers, however, in order to avoid argument and complications, word the label as "containing spices including turmeric."

In another respect the old Federal standard for prepared mus-

tard was even more absurd. The data (mainly Dr. Winton's), upon which the standard was based, were calculated to a *dry*, fat-free and salt-free basis. Also the Massachusetts data on mustard flours and ground seeds (given above) were calculated to a *dry*, fat-free basis. Yet whoever was responsible for the wording of the former standard, used the phrase "calculated free from *water, fat,*" etc., thus not taking into consideration the percentage of acetic acid present (coming from the vinegar) and averaging about 3 percent in the wet paste. Therefore, as it formerly read, this approximate 3 percent of acid must be added to the total solids, from which the fat and salt had been deducted and to which the "carbohydrates," crude fiber and nitrogen were calculated back.

This made the limits of the old prepared mustard standard considerably more liberal than they were intended to be, and as concerns nitrogen and "carbohydrates" the standard was certainly liberal enough, and also for crude fiber in any except an extreme case of a seed containing 7 to 8 percent crude fiber. The author pointed out this oversight in the former prepared mustard standard, in his booklet on the "Federal Spice Standards" nearly twenty years ago, but only recently has the standard been corrected, although most food control chemists calculated the crude fiber, etc., back to a *dry*, fat-free and salt-free basis, as was intended by Dr. Winton, formerly of the Connecticut food inspection laboratory, and others.

The limits shown in Table 49 are those obtained in the analyses of fifteen samples of pure prepared mustard at the Connecticut food inspection laboratory, and twenty by the author.

Table 49. Analyses of Prepared Mustard.

	Percent		
	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Moisture .....	62.10	83.68	78.9
Acidity (as acetic acid) .....	1.80	4.39	3.0
Total solids .....	11.70	34.90	18.1
Fatty oil .....	1.50	10.15	4.4
Nitrogen .....	0.58	0.99	0.77
"Protein" (N x 6.25) .....	3.62	6.22	4.3
Crude fiber .....	0.61	1.83	1.3
Carbohydrates as starch (acid method) .....	1.83	3.12	2.4
Total mineral residue (ash) .....	2.60	8.63	3.6
Salt .....	1.23	6.41	2.5
Ash other than salt .....	0.82	2.22	1.1
Dry, Fat- and Salt-Free Basis			
Carbohydrates as starch (acid method) .....	16.82	24.37	20.15
Crude fiber .....	7.77	*14.12	9.95
Nitrogen .....	*5.12	7.03	6.31

\* Evidently contained an excess of hulls.

Data published recently on some French prepared mustards indicate that "over there" it is customary to manufacture a considerably thicker product, the total solids on eleven brands ranging from 21 percent to 41 percent, with an average of 31.4 percent. The acidity, in terms of acetic acid, ranged from 1.8 percent to 4.8 percent, averaging 3.7 percent. Unless the proportion of volatile mustard oil remaining in the paste is noticeably high, a prepared mustard should contain vinegar to yield about 3.0 to 3.5 percent acetic acid, for preservative purposes.

Rather meagre data on the proportion of volatile mustard oil remaining in prepared mustards indicate that much of it is lost during manufacture and ageing. Any undue elevation of temperature during grinding or exposure to heated air during storage means a loss of this valuable ingredient. Some data, on possibly old samples, showed the volatile oil of mustard in domestic brands to range from 0.01 percent to 0.09 percent. The data on the French pastes, referred to above, showed a volatile mustard oil content from 0.05 percent to 0.25 percent, averaging 0.13 percent. The opinion was given that any good prepared mustard should show at least 0.1 percent.

Sugar is sometimes used in prepared mustard formulæ, but in the author's opinion serves no purpose, except to encourage fermentation.

#### SALAD DRESSINGS

The recent commercial manufacture of "salad dressings" has assumed almost gigantic proportions compared with a decade or so ago. Many wholesale grocers are making a salad dressing for their trade and a number of specialty manufacturers have developed a relatively large business in this product.

As yet, it has received very little attention from the official food inspection chemists or executives. No definite legal standards for either "salad dressings" or "mayonnaise" have been issued and only a few analyses have been published in food inspection literature.

"Mayonnaise," according to standard recipes and dictionary definitions, appears to be well understood as applying to an emulsion made only from eggs, edible oil, vinegar and condimental substances like salt, sugar, mustard and other spices.

"Salad dressing" has been regarded as having a more elastic latitude in composition. No mayonnaise recipe calls for the use of flour, gelatin, gums, starch or artificial color, but in salad dressings one or more of these ingredients are frequently used. Some are made



cold, others cooked more or less, and methods of emulsifying vary in different factories.

To be a satisfactory, successful product, a salad dressing (including mayonnaise) must be a stable emulsion, i.e., one that does not separate at all and allow a layer or even drops of the edible oil to form on top and a layer of water or vinegar to form at the bottom of the container. The conditions necessary to make an oil-water (or vinegar) emulsion that will remain permanent are well known. Water should not be over 15 percent. In addition to the two immiscible liquids, (oil and watery liquid) one of which is to be very finely divided and dispersed in the other, by shaking and beating, there must also be present a third substance, the emulsifying agent, which is usually in colloidal form, or a very fine form of suspension.

In mayonnaise the emulsifying agent is the protein of egg-yolk, known as vitellin, together with some assistance from any egg-white proteins (mainly albumin) that may be present. In cheaper salad dressing mixtures various gums, cooked starch, gelatin, etc., are used as emulsifying agents.

The theoretical aspects of emulsification are somewhat beyond the scope of this article. Those interested in the conditions governing an ideal emulsification in mayonnaise should consult the reports of the "Coöperative Research Committee on Mayonnaise" of the American Home Economics Association, where a large amount of valuable data has been reported.\*

In the manufacture of salad dressings, the use of egg-yolk is preferable to whole egg, as the binding (emulsifying) power of the egg-white is about one-fourth that of egg-yolk, and the egg-white also adds extra water, which is undesirable in some machines that have a tendency to splash. Also the yolk is rich in fatty oil itself and furnishes a good yellow color. However, a small proportion of egg-white mixed with the yolk is desirable for mayonnaise, and would better support any claims of egg (rather than egg-yolk only) being present.

Frozen egg-yolk is made on quite a large scale, especially for the bakery trade, and although there is considerable prejudice among salad dressing manufacturers against using frozen egg-yolks, yet it is mainly uncalled for and there are several distinct advantages, as pointed out by S. K. Robinson in a paper before the Food Section of the April, 1922, convention of the American Chemical Society.

\* See appendix, following the Research on Mayonnaise by Prof. Mark of Simmon's College.

Thus it removes the burden of candling and breaking eggs from the mayonnaise manufacturer; it enables him to have his supply of eggs packed during the months when fresh eggs are the cheapest and best in quality, and a product that can be bought by the pound, instead of varying sized eggs by number or case, presents an economic advantage. Moreover the bacterial content is smaller, thus delaying the decomposition of the protein film adsorbed by the tiny droplets of oil in the emulsion and thus preventing the coalescing of oil droplets and separation of oil.

In the dressings made by Robinson, reported in the above paper, the use of frozen egg-yolk proved entirely feasible, it being practically impossible to notice any material difference between dressings made with fresh egg and frozen egg-yolk, plus a little (10%) egg-white.

The vinegar used in salad dressing is more often a fruit or malt vinegar than that used in catsup and prepared mustard, as the opportunity for vinegar flavor to manifest itself is greater in salad dressings. The edible oil used is nearly always cottonseed oil, which is cheaper and less liable to develop rancidity than olive oil, under the conditions of aëration and oxidation during salad dressing manufacture and storage.

The author has made a number of partial analyses of different brands of salad dressings to furnish data for would-be imitators and found a great variation in oil content and proportion of egg, etc. Recently the U. S. Bureau of Chemistry reported in the *Journal of the Association of Official Agricultural Chemists* for November, 1921, a study, by Dr. H. A. Lepper, of ten brands of commercial origin and one sample of mayonnaise made in the laboratory of the Bureau of Chemistry from a well known recipe.

The sample prepared in the laboratory of the Bureau of Chemistry was in the following proportions: Olive oil, 79.37 percent; cider vinegar, 11.41; sugar, 0.49; salt, 1.08; mustard, 0.59; two egg yolks, 7.06; total, 100 percent.

The attempt to calculate the percentage of egg-yolk from the lecithin-phosphoric acid found on analysis, proved very unsatisfactory, as the data indicated 13 percent egg-yolk as compared with the 7.06 percent actually present. It is evident that more work is necessary on the method of determining this important item before the results obtained with it can be considered as trustworthy. (See below for better results.)

As the egg-yolk contains a large proportion of egg-fat or oil, the total fatty oil found in the analysis of the above laboratory-made

Table 50. Analyses of Salad Dressings and "Mayonnaises."

Label *	Percent									
	Solids (including oil)	Fatty Oil	Total Ash	Salt	Sugar (after inversion)	Unaltered Sucrose	Acetic Acid	Nitrogen	Lecithin- Phosphoric Acid	Starch
Bureau of Chemistry .....	86.26	83.16	1.19	1.09	0.61	0.52	0.51	0.207	0.107	None
Salad Dressing .....	25.63	3.34	3.58	3.32	10.74	1.84	0.86	0.278	0.035	3.08
Mayonnaise .....	56.02	46.93	2.74	2.40	1.78	0.06	0.75	0.318	0.085	None
Mayonnaise .....	88.37	85.22	0.91	0.64	0.44	0.13	0.29	0.218	0.066	None
Mayonnaise .....	88.73	86.02	0.59	0.30	None	None	0.29	0.261	0.081	None
Salad Dressing (Mayonnaise) .....	29.16	6.94	2.95	2.26	11.42	3.09	2.08	0.736	0.128	None
(a Mayonnaise) .....	61.15	36.48	6.39	5.42	11.09	7.26	0.83	0.730	0.085	0.46
Salad Dressing (Mayonnaise) .....	60.94	52.91	3.05	2.40	None	None	1.08	0.593	0.161	None
Mayonnaise .....	59.28	52.83	2.35	2.03	None	None	1.06	0.468	0.095	None
Mayonnaise .....	36.36	12.52	3.15	2.73	12.31	8.62	1.60	0.374	0.106	4.42
Salad Dressing .....	62.33	54.68	3.13	2.65	0.07	None	0.89	0.547	0.145	None
Analyzed by author .....	86.55	81.02	1.51	1.19	None	None	0.60	0.319	None	None
Ditto .....	58.72	52.20	3.40	2.48	None	None	1.32	0.272	None	None
Ditto .....	61.78	55.10	2.88	2.38	None	None	1.22	None	None	None
Ditto .....	63.05	54.90	3.19	2.55	None	None	1.45	None	None	None

\* In the Conn. State Experiment Station Report for 1923 can be found 28 more analyses similar to those given here. Names of brands are given and oil ranges from 4.27 to 87.20 percent. Those containing 75% or more of fatty oil (true mayonnaises) analyzed as follows:

Table 50A. Analyses of Mayonnaise (12 samples)

	Percent		
	Minimum	Maximum	Average
Moisture (water and volatile matter) .....	10.70	15.98	13.19
Total ash (mineral residue) .....	0.59	1.77	1.21
Sodium chloride (common salt) .....	0.30	1.41	0.86
Fatty substances (oil and egg-fat) .....	75.13	87.20	81.83
Acetic acid (from vinegar) .....	0.26	0.60	0.41
Nitrogen (from egg and mustard) .....	0.19	0.44	0.27
Protein (Nitrogen x 6.25) .....	1.19	2.75	1.69
Lecithin-phosphoric acid (from egg) .....	0.02	0.06	0.05

mayonnaise was about 3.8 percent more than the 79.37 percent of olive oil used. The proportions of sugar and salt found were very close to the proportions used and the volatile acidity (as acetic acid) was about what 11.4 percent of cider vinegar of average strength would furnish. The analytical results for the one Bureau of Chemistry-made sample and the ten commercial brands, together with four analyzed by the author in his private analytical practice are given in Table 50.

The figures for nitrogen, in the eleven analyses reported by Lepper, should be due to the protein of the egg-yolk (or whole egg as used by some manufacturers) plus the proteins and other nitrogen-containing constituents of mustard and other spices. Any addition of gelatin would considerably increase the nitrogen figure.

The total ash (residue on careful burning) includes the salt; and the difference between the percent total ash and percent salt is due to mineral salts in the egg-yolk and spices, or gums or cereal products, if present. Starch was found present in three samples, indicating the use of starch or cereal flour as filler or thickener.

It is significant that the three samples containing starch in some form contained much less fatty oil than the other samples, excepting one sample with only 6.94 percent fatty oil, which may have been thickened with gelatin, as the nitrogen figure was very high, or with gum as stated on the label. This sample was boldly labeled "Mayonnaise," but can be considered only as a crude imitation of genuine mayonnaise. This judgment is true also of the sample containing 12.52 percent oil and 4.42 percent starch, which is labeled "Mayonnaise." The sample containing 36.48 percent oil and 0.46 percent starch is not entitled to the name "Mayonnaise," either.

The water, plus the volatile acetic acid (from the vinegar), in the samples reported, ranged from 11.27 percent to 74.37 percent, truly a remarkable variation, and affording some idea of comparative manufacturing profits. If the generally understood definition of mayonnaise be accepted, the only water present should be that coming from the vinegar used, plus a small amount from the egg material. A minimum limit of 75% fatty oil is logical.

Only two of the commercial brands reported by Lepper come up to this standard, both being properly labeled "Mayonnaise." The more elastic name of "Salad Dressing" allows more or less water from other sources, but it would seem desirable that even here a legal limit be fixed, for instance not over forty percent water, other than that coming from ten percent of vinegar. It seems only rea-

sonable to expect that half the product be oil, egg-solids, sugar and spices. Sugar, in the samples reported by Lepper, ranged from none, or a fraction of one percent, to as high as 11 percent, it being more or less inverted already by the cooking with vinegar acid. Unaltered sugar was present in two rather low grade products in the proportion of 7.26 percent and 8.62 percent, in each case being roughly about two-thirds of the sugar originally used. In the two lowest grade samples (3.34 percent oil and 6.94 percent oil) about 10 or 11 percent sugar had been used also. None of the samples containing 45 to 80 percent salad oil contained any appreciable amount of sugar.\*

As to spices, mustard is of course indispensable and a great variety of others are used in getting "bouquet" and characteristic flavors. Turmeric is a well known spice, universally used in curry and other dressings, but the yellow color of this spice should not be the only source of yellow color in the product, in other words, much of the yellow color should come from egg-yolk. One sample reported by Lepper (3.34% oil) was colored with a yellow coal-tar dye!

Ultimately we shall have legal definitions and standards for salad dressings and mayonnaise, as we already have for prepared mustard, and meanwhile the trade can largely determine what those standards will be, by bringing about some uniformity in the products; in other words by establishing an acceptable, fair trade standard, which the Government food inspection authorities will feel justified in adopting. This has been the genesis of many of our official food standards.

In the November, 1923, issue of the *Journal of the Association of Official Agricultural Chemists*, A. E. Paul, reporting as referee on "spices and other condiments," describes an experiment similar to Lepper's, wherein a salad dressing was made from a formula which on the percentage basis figured out as follows:

	Percent
Fatty oils (olive, peanut and cottonseed).....	82.62
Vinegar .....	8.62
Mustard .....	0.61
Sugar .....	0.50
Salt .....	1.11
Egg-yolks (12) .....	6.40
Preservative .....	0.14
	<hr/> 100.00

This mixture would yield approximately 88.5 percent total solids (including oils); about 85 percent of fatty material (including fat from

\* Sugar has been found to encourage fermentation and spoilage.

egg-yolks); about 0.47 percent total acid (as acetic acid from vinegar); about 0.055 of lecithin-phosphoric acid (from egg-yolks) equivalent to 3.2 percent dried egg-yolk solids, or 6.4 percent fresh egg yolks.

The salad dressing was analyzed by three experienced analysts with the following results:

	A	B	C
Total solids (incl. oil) .....	88.98	89.75	88.89
Sugar .....	0.40	0.39	0.58
Total acid (as acetic) .....	0.46	0.47	0.44
Fatty oils .....	85.91	86.06	82.51
Lecithin-phosphoric acid .....	0.054	0.058	0.058
Equivalent to fresh yolks .....	6.33	7.05	7.05
Equivalent to yolk solids .....	3.20	3.44	3.44

In contradistinction to Lepper's results it will be seen that the estimation of the proportion of egg-yolks from the lecithin-phosphoric acid content was satisfactorily close. This is perhaps the most important test in the official analysis of a salad dressing, especially if a standard is adopted calling for a legal minimum of egg material, and the experiments show that the egg material (whether whole egg or egg-yolk) can be closely approximated.

#### "WORCESTERSHIRE" SAUCE

This product, so Anglo-Saxon in name, but largely Oriental in makeup, is to be found upon nearly every dinner table in English speaking countries.

The "nobleman in the country," whose "recipe" is the basis of the original sauce, as first made in England, must have been a traveled individual, to whom the universal food sauce of China and Japan appealed, but who, like most noblemen, wanted such a sauce hot and spicy.

Therefore the delicate-flavored soy sauce, which is the principal and most characteristic ingredient of "Worcestershire Sauce," was vinegared and strongly peppered, with the result that we have a product of much less universal use than might be the case.

The vinegar used in the original recipe was presumably malt vinegar and some of the better grades of "Worcestershire Style Sauce" (to use the legally correct title for other than the original product) made in this country are made with malt vinegar, but more often a well flavored grain or spirit vinegar is substituted.

A number of analyses indicate the finished sauce to contain about 3 percent of acetic acid, showing the use of an approximately 60

"grain" vinegar to thin down the thick soy sauce which is the characteristic basis of "Worcestershire Style Sauce" and similar differently named products.

The peppering is usually overdone and the other possible ingredients ("fruit products" as some claim) are of little consequence, except possibly tamarind, but in soy sauce itself we have one of the most interesting and fascinating food products in the world, the universal food flavoring agent used by millions of Asiatics, and made and consumed in immense quantities.

Those interested in the complex fermentation and technique involved in the manufacture of soy sauce and a number of related soy products, such as "miso" (a thick soup-stock), "tofu" (a sort of soy bean cheese), "natto" (another cheese) and soy bean milk, should consult the recent valuable bulletin (No. 1152) prepared by Dr. Church of the U. S. Department of Agriculture, Bureau of Chemistry. Here we will confine ourselves to soy sauce itself and quote as follows from the above mentioned bulletin:

"Soy sauce is a dark-brown salty liquid made by the fermentation of soy beans with, as a rule, some additional starchy component. It is widely used as a seasoning throughout Japan, China and Java, and has been introduced into the Philippines and Hawaii. Where the occidental would use a vegetable or meat extract and salt, the oriental daily uses soy sauce. Americans are familiar with soy sauce as it is used in Chinese-American ("Chop Suey") restaurants and as the ingredient which produces the characteristic flavor of the Worcestershire type of sauce. The increasing popularity of highly seasoned foods in the United States may reasonably be expected to develop the use of soy sauce and of table sauces having a flavor more positively that of the ingredient, soy sauce.

"The soy bean, an annual leguminous plant, native to south-eastern Asia, has been cultivated in the East for more than 5,000 years. Rich in protein and oil, though deficient in starch, it has been used as a food and for technical purposes. . . .

"The process of manufacture which produces soy-bean sauce, or, as it is called in Japan, sho-yu, begins with the preparation of the ingredients and includes a preliminary mold fermentation, followed by a ripening in brine. . . .

"The mold-fermented material is emptied into the strong brine, thus producing a mash. Constant daily attention is given to aëration, even distribution and stirring of the solid ingredients. Progressive changes take place over a period of from six months to

several years, until at last mature 'moromi,' as the mash is designated by the Japanese, is produced.

"The rather thick, dark-brown mash resulting is siphoned or pressed to produce the soy sauce, which is brought to a boil, filtered, and in the more modern of the Japanese factories processed or partially pasteurized. The completed sauce is distributed in casks or bottles."

The Japanese product is generally considered superior, being more commercially standardized and scientifically made, but at the best soy sauce varies much in composition, according to the locality and process of manufacture.

The analyses of soy sauce given in Table 51 are by Dr. Loomis of the U. S. Department of Agriculture, Bureau of Chemistry, and are in terms of grams per 100 cubic centimeters. It will be noticed that more than half of the solids is salt.

Table 51. Analyses of Soy\* Sauce.

Grams per 100 Cubic Centimeters										
		<i>Specific Gravity</i>	<i>Total Solids</i>	<i>Reducing Sugars</i>	<i>Total Ash</i>	<i>Salt</i>	<i>Salt-Free Ash</i>	<i>Total Nitrogen</i>	<i>Acidity (as lactic acid)</i>	<i>Alcohol (by volume)</i>
Japanese	soy...	1.184	33.86	1.68	20.00	18.53	1.47	1.30	0.76	1.02
"	" ..	1.176	32.52	2.70	17.94	16.28	1.66	1.25	0.68	0.75
"	" ..	1.196	37.69		20.10			1.37		
Chinese	soy...	1.259	47.04	10.57	26.84	25.74	1.10	0.77	0.67	none

\* Soy beans average: Moisture 9.9 percent, Ash 5.3 percent, "Protein" (N x 6.25) 36.5 percent, Fiber 4.3 percent, Fatty oil 17.5 percent, Carbohydrates, etc., 26.5 percent.

Further tests showed the nitrogen to be in the form of ammonia and amino compounds mainly, as would be expected from a raw material rich in protein which had undergone a lengthy fermentation process. In several respects soy sauce may be considered as a sort of vegetable "beef extract"; and would, to a certain extent, have a similar stimulating effect when used as a seasoning on various foods.

The proportion of soy sauce used in Worcestershire sauce varies, with the ideas and generosity of various condiment manufacturers. Only a very few limited analyses have been made. The Connecticut State Experiment Station, in 1911, reported on six brands (four English and two American) showing the acidity (as acetic acid) to range from 1.38 percent to 3.72 percent, with polariscopic data indicating more or less sugar (especially reducing sugars) to be present. The writer has analyzed the leading English brand and one of the best American brands, with the results shown in Table 52.



Table 52. Worcestershire Sauces.

	Percent	
	<i>English</i>	<i>American</i>
Acidity (as acetic acid) .....	3.10	3.45
Total solids .....	27.17	26.59
Total ash .....	5.98	5.63
Salt .....	3.62	3.94
Salt—free ash .....	2.36	1.69

No legal standard for Worcestershire sauce has been fixed as yet.

## Chapter V.

### The Legal Chemistry of Edible Oils.\*

#### GENERAL COMPOSITION AND ANALYTICAL CONSTANTS

Under the heading "Edible Vegetable Oils and Fats" the Federal food standards (Circular 136, Office of Secretary, U. S. Department of Agriculture) define such products as "glycerids of the fatty acids as are recognized to be wholesome foods, and are dry and sweet in flavor and odor." By "glycerids" is meant the glycerol esters of various fatty acids, such as stearic acid, palmitic acid, oleic acid, linoleic acid, arachidic acid, myristic acid, lauric acid, lignoceric acid and others. These glycerol esters of fatty acids are sometimes called "stearin," "palmitin," "olein," etc., according to which fatty acid is present, and, as there are three similar replaceable groups of atoms in glycerol to be replaced by fatty acid atom groups, we can have monostearin, distearin and tristearin, etc.; also mixed esters where two or even three different fatty acid atom groups are present as, for instance, monostearin-dipalmitin. Ordinary "stearin" is the tristearin, "palmitin" is the tripalmitin, "olein" the triolein, etc. A more correct name for these esters formed by the chemical combination of glycerol and fatty acids, would be along the lines of the simpler esters, thus "stearin" (tristearin) is glycerol tristearate, analogous to ethyl stearate, etc., etc.

Stearin and palmitin are solid fats and olein is a liquid fat. The consistency of any fat or fatty oil depends upon the preponderance of solid or liquid glycerol esters. Each edible oil is composed of a mixture of the glycerol esters of several different fatty acids; there is present also usually a little free fatty acid, resulting from the action of fat-splitting ferments, or enzymes, (olease for instance) present in the fruit or seed from which the oil has been pressed. The more clean and sound the source of the oil, and the more clean and rapid the process of pressing and cooling, the less free fatty acid there will be in the edible oil. This is a very important item (in analysis

\* Originally published in *The Spice Mill*, July, 1923, *et seq.*

or commercial selling) as the development of rancidity is largely due to oxidation of free fatty acids, under the influence of air, heat and sunlight, and it follows to some extent that the less free fatty acid there is present in the oil, the less rancid it will become ultimately. Some recent investigations indicate that the glycerol esters themselves can oxidize, under certain conditions, to form rancid tasting products; however, the trade are well justified in their habit of judging the quality of an edible oil considerably, from the proportion of free fatty acids present.

Upon the saponification of fats with alkalies, glycerol is reformed and the alkali metal unites with the fatty acid atom group to form a metallic salt known as "soap." Potassium (the metal in caustic potash) forms a "soft soap" usually, while the various "hard soaps" contain the metal sodium from caustic soda.

Edible fats and oils always contain a small proportion of matter which is not capable of being saponified and is reported in any analysis as "unsaponifiable matter." In animal fats this unsaponifiable matter is mainly cholesterol, and in vegetable fats and fatty oils it is variously called phytosterol or sitosterol and probably plays some important part in stabilizing the emulsion form in which practically all fats exist while in the plant or animal. By a study of the crystal form of the "unsaponifiable matter" obtained from a suspected fat or oil, it can be shown a vegetable oil is adulterated with an animal fat, or vice versa, as cholesterol especially forms a very characteristic crystal, recognizable under the microscope.

In comparatively few cases is the exact composition (i.e., the exact identity and proportion of the various glycerol esters present) of edible fatty oils known; and to separate, identify and estimate these esters, or their corresponding fatty acids, in any sample would be a monumental task. Hence, in an analysis of a fatty oil, certain "constants" are determined to see if they are normal for the supposed oil in question, or suggestive of some adulterating oil instead; certain oils are tested for direct by color reactions with various reagents, others by separating some free fatty acid characteristic of the oil (i.e., arachidic acid as proof of arachis or peanut oil) and by a study of the "unsaponifiable matter," as mentioned above. Mineral oils would appear as "unsaponifiable matter" also, in analysis, and would greatly increase the usually very low figure (less than 1%) for that item.

The constants may be determined on the fatty oil as a whole, or on the liberated free fatty acids, obtained by saponifying the oil

with an alcoholic solution of caustic soda or potash and liberating the free fatty acids from the "soap" formed, by action of a strong mineral acid. The chief constants in use are the "specific gravity," or the weight of the oil as compared with an equal volume of distilled water; the "melting point," or the exact temperature of the melting of a solid fat or fatty acid; the "solidifying point" of a liquid fat or fatty acid; the "iodine absorption," or percent of iodine absorbed under certain conditions; the "acid number," or the number of milligrams of potassium hydrate required to neutralize the free fatty acid in one gram of the oil and from which the percent of free fatty acid can be calculated; the "saponification number" (see below), and, in addition, there are several others occasionally made use of in examining fatty oils and fats, viz.: "index of refraction," or the measurement of the degree of deflection caused in a ray of light in passing from one transparent medium into another; "butyro-refractometer reading," or the expression of the same on the arbitrary scale of a refractometer especially designed for butter; "Maumené number," or the rise in temperature upon mixing a definite quantity of the oil with a certain quantity of strong sulfuric acid; and the "specific temperature reaction," or the above rise in temperature compared with the rise in temperature in an equal volume of water under the same conditions.

Table 53 gives the values for various constants as determined and compiled by Tolman and Munson of the Bureau of Chemistry, U. S. Department of Agriculture. The results obtained in the Bureau of Chemistry laboratories are for normal edible oils, hence the range of variation is usually less than in the compiled results, where many oils unfit for food purposes, or at least quite abnormal, are reported. In the determination of the specific gravity, for instance, the amount of free acid present is a very important consideration and one which would doubtless explain some of the abnormal results in the compiled data.

The constants of the free fatty acids resulting upon saponifying a fat or fatty oil with alkali and decomposing the "soap" formed usually refer to the solid and liquid acids combined, although some of them can be determined for a specific group of acids or even a single acid if necessary. The "iodine absorption" of the fatty acids and their melting point are the constants most frequently determined. The solidifying point of the melted acids, which is also occasionally noted, is usually somewhat lower than the melting point.

Table 53. Analytical Constants of Certain Oils and Fats.

Oil or Fat	Specific Gravity (15.5° C.)		Melting Point of Separated Fatty Acids		Saponification Numbers	
	Bureau of Chemistry Results		Bureau of Chemistry Results		Bureau of Chemistry Results	
	Chemistry Results	Compiled Results	Chemistry Results	Compiled Results	Chemistry Results	Compiled Results
California olive oil.....	0.9162 to 0.9180	0.9140 to 0.9185	19.2 to 81.0° C.	21.0 to 28.0° C.	189.3 to 194.6	187.0 to 193.5
Italian olive oil.....	0.9155 to 0.9180	0.9158 to 0.9180	21.6 to 29.3	23.7 to 29.0	189.7 to 192.0	185.6 to 192.3
Spanish olive oil.....	.....	0.9169 to 0.9172	.....	24.0 to 26.0	.....	.....
Algerian olive oil.....	.....	0.9170 to 0.9196	.....	24.8 to 38.0	.....	.....
Cottonseed oil.....	0.9226 to 0.9236	0.9160 to 0.9362	35.5 to 39.6	32.0 to 43.0	196.0 to 198.5	191.0 to 196.6
Maize or corn oil.....	0.9233 to 0.9256	0.9213 to 0.9255	21.6 to 23.0	16.0 to 22.4	189.9 to 193.4	184.0 to 193.4
Arachis or peanut oil...	0.9186 to 0.9188	0.9110 to 0.9220	33.2 to 37.6	26.0 to 36.4	188.8 to 190.0	184.3 to 196.0
Sesame oil.....	0.9218	0.9200 to 0.9250	27.4	21.0 to 40.0	174.1 to 176.6	167.7 to 183.0
Rape or colza oil.....	0.9143 to 0.9163	0.9112 to 0.9184	20.0 to 21.9	15.5 to 22.0	174.1 to 176.6	167.7 to 183.0
Lard oil.....	0.9148 to 0.9175	0.9150 to 0.9160	33.2 to 38.4	33.0 to 38.4	195.3 to 197.7	189.5 to 196.0
Almond oil.....	0.9108 (25°)	0.9154 to 0.9200	.....	12.0 to 14.0	189.5 to 192.5	184.0 to 191.7
Sunflower oil.....	0.9239 to 0.9244	0.9240 to 0.9262	.....	17.0 to 24.0	191.2 to 192.3	184.0 to 197.6
Poppy-seed oil.....	0.9147 to 0.9193	0.9240 to 0.9370	25.4 to 25.8	20.0 to 21.5	190.2 to 193.8	179.8 to 194.0
Mustard oil (fatty).....	0.9259 to 0.9269	0.9125 to 0.9183	20.8 to 21.5	15.0 to 21.5	173.0 to 182.8	170.2 to 174.0
Coconut oil.....	.....	0.9250 to 0.9260	.....	24.0 to 27.0	.....	.....
Palm oil.....	.....	0.9210 to 0.9460	.....	47.8 to 50.0	.....	.....
Linseed oil.....	.....	0.9315 to 0.9347	.....	49.2	.....	.....
Magnolia oil.....	0.9128 to 0.9130	0.9315 to 0.9347	34.3 to 38.2	17.0	189.2 to 189.5	184.0 to 191.0
Cocoa butter.....	.....	0.9450 to 0.9760	.....	48.0 to 53.0	.....	.....
Lard.....	.....	0.9310 to 0.9380	.....	35.0 to 47.0	.....	.....
Soy bean oil.....	.....	0.9203 (25°)	.....	.....	.....	.....
Beef tallow.....	.....	0.9249 (15°)	.....	.....	.....	.....

Table 53. Analytical Constants of Certain Oils and Fats.—(Continued)

Oil or Fat	Iodine Absorption		Iodine Absorption of Separated Fatty Acids		Butyro-Refractometer Reading at 15.5° C.	Index of Refraction at 15.5° C.	Mauenné Number	Specific Temperature Reaction
	Bureau of Chemistry Results	Computed Results	Mixed Acids	Liquid Acids				
California olive oil...	78.5 to 89.8	77.7 to 93.5	86.0 to 90.0	88.9 to 100.0	66.9 to 69.2	1.4703 to 1.4718	42.5 to 52.0	94.7 to 109.7
Italian olive oil...	79.2 to 86.1	79.0 to 89.8	.....	.....	67.3 to 68.5	1.4706 to 1.4713	42.5 to 49.1	95.6 to 104.7
Spanish olive oil...	.....	84.1 to 84.5	.....	.....	.....	.....	.....	.....
Algerian olive oil...	.....	79.3 to 89.5	.....	.....	.....	.....	.....	.....
Cottonseed oil...	103.8 to 110.9	106.5 to 110.7	111.0 to 116.0	136.3 to 141.5	72.3 to 75.6	1.4737 to 1.4757	66.2 to 73.4	172.4 to 191.1
Maize or corn oil...	116.7 to 123.3	111.1 to 123.9	113.0 to 125.0	126.6 to 134.5	75.6 to 77.5	1.4757 to 1.4768	75.2 to 89.2	190.2 to 212.5
Arachis or peanut oil	87.8 to 96.3	85.6 to 105.0	95.0 to 103.0	.....	70.0 to 71.3	1.4723 to 1.4731	61.0 to 67.8	135.5 to 140.2
Sesame oil	.....	102.0 to 112.0	109.0 to 112.0	115.4	73.3	1.4742	61.8	170.3
Rape or colza oil...	92.5 to 101.2	94.1 to 106.2	99.0 to 105.0	105.1	74.1 to 74.8	1.4748 to 1.4752	54.5 to 67.8	135.0 to 152.5
Lard oil	.....	60.0 to 82.0	64.0 to 81.0	104.0	68.8 to 69.5	1.4702 to 1.4720	46.5 to 47.8	103.3 to 106.2
Almond oil	.....	96.2	.....	.....	.....	.....	.....	.....
Sunflower oil	104.1 to 108.3	119.0 to 135.0	.....	.....	72.7	.....	45.3	117.6
Poppy-seed oil	135.2 to 134.9	130.5 to 141.0	.....	.....	77.8	.....	60.0	166.7
Mustard oil	98.4 to 113.0	92.1 to 106.5	.....	.....	74.5 to 76.5	1.4750 to 1.4762	75.8 to 85.5	213.0 to 237.0
Coconut oil	.....	8.0 to 9.5	.....	.....	.....	.....	61.0 to 70.4	130.9 to 190.3
Palm oil	75.3 to 53.0	84.0 to 9.5	8.4 to 9.3	31.9	49.1	.....	91.0	44.0
Linseed oil	.....	51.0 to 52.5	.....	.....	.....	1.4587	.....	.....
Magnolia oil	179.5	171.0 to 181.0	155.0 to 182.0	.....	60.1 to 70.0	1.4690 to 1.4777	103.0 to 126.0	.....
Cocoa butter	76.1 to 81.7	.....	.....	.....	94.5 to 65.0	1.4988 to 1.4991	.....	.....
Lard	.....	32.0 to 41.7	32.5 to 39.1	.....	46.0 to 47.8	1.4565 to 1.4578	.....	.....
Soy bean oil	.....	50.0 to 70.4	64.0 to 81.0	104.0	44.8 to 53.0	1.4537 to 1.4613	24.0 to 27.5	.....
Beef tallow	.....	128.0 to 134.0	.....	.....	.....	1.4734 to 1.4741	.....	.....
	.....	38.0 to 46.0	.....	.....	49.0	.....	.....	.....

The iodine absorption data in the table were taken in part from Leffman and Beam's "Food Analysis."

The "saponification number," sometimes called the "Koettstorfer number," is the number of milligrams of potassium hydrate needed to saponify 1 gram of the oil or fat. In the table the compiled data for the last six oils and fats were taken from Lewkowitsch, "Chemical Analysis of Oils, Fats and Waxes."

The butyro-refractometer reading and the index of refraction are practically two expressions for the same phenomenon and the latter may be readily calculated from the former. In the table the data for the last three oils and fats were taken from Lewkowitsch.

The rise in temperature with sulfuric acid, and this value compared with water under the same conditions, usually known as the "Maumené number" and the "specific temperature reaction" respectively, are also closely related constants. The results shown in the table, with a few exceptions, are from Tolman and Munson's report on olive oil substitutes, previously referred to.

### OLIVE OIL

This oil, so highly prized for salad and other food purposes, is obtained, by pressure or extraction, from the ripe fruit of the olive tree (*Olea europæa sativa*), of which three hundred varieties are to be found in Italy alone. For many years Italy led in the commercial production and exportation of olive oil, but now Spain is assuming the lead, due to a bigger supply of trees and oils to select from and to the introduction of modern clean factories and apparatus. France produced only a very small proportion of the olive oil she exported, most of it coming originally from Spain, Italy or Algeria.

The Spanish oils shipped to America are particularly high grade, usually running very low in the proportion of free fatty acids and being generally more free from incipient rancidity than Italian oils. The Spanish oils are usually of a golden yellow color, very bland and mild flavored. From a golden yellow the color of olive oil ranges to a light yellow with greenish tinge and in some cases to even a dark green color, due normally to dissolved *chlorophyll*, the coloring matter of leaves and green fruits.

The quality of an olive oil depends upon various conditions of manufacture and storage. Oils intended for salad or general food purposes are always expressed cold. As pointed out earlier, the

proportion of the free fatty acid (mainly oleic acid) depends upon how much opportunity there has been for the action of a fat-splitting enzyme or ferment, in the bruised fruit, to act upon the oil before or during pressing, or afterwards if the oil has not been properly clarified. The more sound and fresh the fruit and the more rapid the pressing and cooling and clarifying operations, the less free acid there will be found. Many of the better oils now being shipped, especially from Spain, are appearing on the market with considerably less than one-half of one percent of free fatty acids. Above three percent free fatty acid renders an oil inedible, and much less than that proportion, when oxidized by exposure to air, heat or sunlight, will cause a degree of rancidity which becomes objectionable to many people. The average content of free fatty acid (as oleic acid) in about one hundred olive oils, tested by the author in recent years, is 1.1 percent, ranging from 0.34 percent to 2.3 percent.

The Federal food standards (Circular 136, Office of Secretary, U. S. Dept. of Agriculture) merely defines olive oil as "the edible oil obtained from the sound, mature fruit of the olive tree," and fixes no limits on the proportion of free fatty acid, or other analytical items. The latter, however, will be normal if the oil is pure, and any abnormality, unless satisfactorily explained, is considered proof of adulteration.

A recent Service and Regulatory Announcement (Chemistry, No. 28) says: "The use of wholesome vegetable oils other than olive oil for salad purposes has become widespread. The term 'salad oil' is no longer indicative of olive oil exclusively. In the absence of any statement, design or device on the labels conveying directly or by implication any false or misleading impression concerning the origin or characteristics of the product, no objection will be made to the designation of edible vegetable oils other than olive oil as 'salad oil,' with or without qualification." Quite a few prosecutions have been carried through the courts because cans or bottles of other vegetable oils were labeled with designs showing olive trees, etc., or scenes from countries producing olive oil only.

Food Inspection Decision, No. 139, issued in 1912, says: "A careful consideration of the subject leads to the conclusion that the only oil to which the term 'sweet oil' may be correctly applied is olive oil." It is held, therefore, that any oil other than olive oil is misbranded when sold under the name "sweet oil." It is not correct, for example, to label cottonseed oil as "sweet oil" and then elsewhere on the label to describe correctly the true character of the oil.



Small proportions of olive oil are frequently mixed with cottonseed and other oils and then sold as a "compound." A Service and Regulatory Announcement (Chemistry 24) says: "Any ingredient mentioned on the label of a compound should be present in sufficient quantity to definitely impart its characteristics to the product. Cottonseed (or other edible) oils to which only a sufficient proportion of olive oil has been added to impart an olive-oil flavor may properly be labeled as 'cottonseed oil flavored with olive oil,' or some similar term. Such a product, however, should not be labeled as a compound of cottonseed and olive oils."

The old Federal standard for olive oil fixed limits for the refractive index and called for an iodine absorption between 79 percent and 90 percent.

Pure olive oil contains about 28 percent of the solid glycerol esters, consisting of palmitin and traces of arachidin or the glycerol ester of arachidic acid. The remainder is mainly a mixture of the glycerol esters of oleic and linoleic acids in the proportion of 93 parts of the former to 7 parts of the latter. About 1 percent of "unsaponifiable matter" is usually to be found, consisting mainly of phytosterol. Free fatty acid, as said above, is always present, being dependent upon various factors. Munson and Tolman, in the examination of 185 samples of commercial oils and olive oils of known purity, found an average of 1.65 percent of free fatty acids (calculated as oleic acid), the maximum and minimum being 8.21 percent and 0.20 percent, respectively.

Olive oil, on account of the comparatively high price which it commands, is extensively adulterated with and often entirely substituted by foreign oils, either singly or mixed. The adulterants usually used in this country are cottonseed oil, maize or corn oil, soya bean oil and arachis or peanut oil. Oils from abroad may contain sesame oil, rape or colza oil, poppy-seed oil and, very rarely, fatty mustard oil, which has been used to adulterate rape oil. Lard oil also is sometimes used to adulterate olive oil. The green color of certain olive oils (due to chlorophyll) is occasionally imitated by the addition of coloring matter, sometimes of a mineral character. Copper acetate has been reported as being used for this purpose, but it is more likely that some natural or artificial organic color is used.

**Changes in Olive Oil After Long Standing.** Olive oil, although the best known and most desirable edible oil, is, unfortunately, one of the oils most subject to oxidation and other changes which develop

rancidity. The principal factor is oxygen; indeed it has been said that without oxygen there can be no rancidity. However, other factors, such as light, heat, moisture and contact with metals, serve to accelerate the oxidation. The chemical reactions involved are rather complex and some of the products formed have a very disagreeable taste or odor, while others do not seem to be responsible for the effects known under the term "rancidity."

In earlier years it was supposed that the principal changes consisted of the slow liberation of free fatty acids from the glycerol esters constituting the oil, due to a fat-splitting ferment or enzyme (olease or lipase) naturally present or formed by bacteria allowed to get in during careless manufacture; and subsequently the oxidation of the free fatty acid to oxyacids having disagreeable taste, etc. Oleic acid is the principal fatty acid (combined with glycerol as an ester and called "olein" or "triolein") in olive oil and, being an "unsaturated" acid capable of uniting directly with iodine (hence the analytical item known as "iodine absorption" or "iodine number") and other elements, it takes up oxygen readily. Oleic acid when fresh is white, tasteless and odorless, but quickly becomes yellow in color and acquires a rancid odor from oxidation. Thus the present commercial practice of requiring a very low content of free fatty acid in edible oil is well founded, as it stands to reason that the less free acid there is present to start with the less rancidity there will be when ageing has enabled oxidizing changes to take place. It must be remembered, however, that the proportion of free fatty acid can in time increase, due to the aforementioned ferment or enzyme naturally present and especially that formed by bacteria present as the result of careless manufacturing methods.

The percent of free fatty acid is not a measure of rancidity, as freshly liberated oleic acid is not rancid (as said above) and, if the oil is well protected from oxidation, an oil with a 1 percent free fatty acid content can remain "sweet" while a carelessly protected oil with only 0.5 percent acidity may become quite objectionable. However, on general principles, the less free fatty acid there is present the better. More recently it has been determined that other compounds than the oxidized free fatty acid are formed by the combined effects of oxygen, light, moisture, etc., some of which are also disagreeable tasting and smelling substances. Various aldehydes, ketones and acids of less molecular weight than the fatty acids originally present, are formed and appear to be constant constituents of fats and fatty oils which have stood too long under unfavorable conditions and become rancid. Most of the various color-forming tests used for the detection of incipient or masked

rancidity ("Kreis rancidity test," for instance) depend on the presence of several or all of these various constituents resulting from oxidation changes, and it is to the effect of all of them, including the oxidized free fatty acid, that the characteristic odor and taste of rancid fats and oils are due.

The development of rancidity in a carefully manufactured and properly stored olive or other edible oil is very slow, especially if the percent of free fatty acid be low to start with. In a grocery store where turnover of stock is frequent, a good olive oil, even though stored in glass and exposed to light on a shelf, will test normal and show no very objectionable rancidity. In sealed tin cans it will keep "sweet" for a relatively long time. However, there are stores in certain sections where olive oil is infrequently asked for and a small batch of bottles may stand exposed to light for a year or so, or one or two bottles may be shoved in back of a new shipment or otherwise get displaced so as to stand many years. There is always an air space in the neck of each bottle, one-fifth of which is oxygen; moreover, there is more or less dissolved air and oxygen in the oil and for the small amount of oxidation necessary to render an oil rancid and to make it analyze abnormally in time, this is sufficient.

How abnormal an old olive oil sample can analyze will be illustrated below with data on a pure oil, originally normal in every way and of very excellent quality, with a very low content of free fatty acid to start with. An oil showing less change than this particular oil would be found to analyze so abnormal as to lead to the charge of adulteration unless the official chemist studied into the matter very thoroughly.

The oil in question was one of the first commercial olive oils produced in California, being carefully pressed from selected olives grown on the Windermere Ranch of Mr. Andrew McNally at La Mirada, Cal., and sold through their Eastern office in the Rand, McNally Building in Chicago. The author was called upon to analyze this oil in the Fall of 1906 and found it to be a pure, very high grade olive oil, testing as given below. On account of it being the first California olive oil which the author had knowingly tested and because of the rather attractive bottle, it was allowed to stand year after year on an exhibition sample shelf to the present day (1927), being kept corked, but exposed to indirect light and room temperature meanwhile. It was analyzed a second time in 1916 and more recently in 1926 as follows:

In 1916 an official analysis would have resulted in this oil being declared "adulterated," in fact, probably at the end of five years the regular data would have been found to be suspiciously abnormal. The

	1906	1916	1926
Odor and taste .....	No rancidity	Very rancid	Extremely rancid
Kreis rancidity test .....	.....	Positive	Very strong
Specific gravity (15.5° C) .....	0.9132	0.9254	0.9383
Iodine absorption number .....	83.60	75.26	68.58
Saponification number .....	190.80	199.60	213.20
Acid number (from percent free acid) .....	0.96	8.04	15.68
Ester number (Sap. No.—Acid No.) .....	189.84	191.56	197.52
Free fatty acids (as oleic) .....	0.48%	4.02%	7.84%

lowering of the iodine absorption value is due, no doubt, to the satisfaction by oxygen of the normal affinities for iodine of the "unsaturated" oleic and other fatty acids present. The acidity (and acid number) has increased about sixteen-fold and undoubtedly much more liberated free fatty acids have been changed to non-acid substances, possibly ketones and aldehydes. Just why the ester number (and incidentally the saponification number) has increased is not so plain, in view of the fact that there must have been a great loss of glycerol esters during the liberation of free fatty acids.

The data suggest that a hasty condemnation of an old olive oil as "adulterated" is possible and that the history of an abnormally testing oil should be ascertained before prosecution is started.

#### COTTONSEED OIL

Cottonseed oil is obtained by pressure from the seeds of different species of *Gossypium*, the most common species being *G. herbaceum*, L. The oil intended for food purposes is expressed cold and in the crude state has a color ranging from red to a reddish black. It is refined by alkali treatment and when intended for use as salad oil, is allowed to stand in chilled tanks until the "stearine" or solid fatty matter has separated out. The refined oil has a yellow color and pleasant nutty flavor. It is used extensively as an olive oil substitute and adulterant, and in the preparation of oleomargarine, "compound lard" and lard substitutes. Practically all oil now sold as "salad oil" is composed of cottonseed oil and it is by far the commonest adulterant found in lard. The various "cooking oils" are composed of cottonseed oil principally. Its cheapness renders it little subject to adulteration.

Cottonseed oil is composed principally of the glycerol esters of stearic and palmitic acids and oleic and linoleic acids, the esters of the latter acids having a ratio to each other of 3 and 4.5 respectively. It also contains about 3.5 percent of oxy-acids. The alkali treatment referred to above removes practically all free fatty acids. Tolman

and Munson found 2.17 percent of free fatty acids in a freshly expressed, unpurified oil.

A very delicate test for the presence of cottonseed oil is the so-called "Halphen test." The fat of animals fed on cottonseed products will sometimes give a very faint reaction even. Heating the oil to 250° C. for a short time weakens the Halphen reaction and longer heating may entirely destroy it. Fortunately, however, the color tests due to the action of nitric acid or that of nitric acid and albumen ("Brullé test") are not affected nor are the constants to any great extent. The liberated fatty acids of cottonseed oil also respond to the above tests.

Cottonseed "stearine" occurs as a by-product in the refining of salad oils, being deposited in the tanks upon standing or obtained more quickly by cooling the oil and pressing after the alkali treatment. It contains but little pure *stearin*, being composed principally of *palmitin*. It is used in the manufacture of butter and lard substitutes and responds to the various color tests mentioned above.

#### MAIZE OR CORN OIL

This oil has come into prominence during the last ten years and, like cottonseed oil, was originally only a by-product. It is present only in the germ portion of corn, the germ being more than half oil; but in the entire kernel it figures out but from 3 to 6 percent. Were it not for the fact that, in the manufacture of cornstarch and "grits," etc., the germ is more or less completely separated out, it would not pay to extract the oil.

There are two processes ("wet" and "dry") for removing the germs, the better oil resulting when the dry process is used. Corn oil is therefore obtained by pressure from the germs of the seed (kernels) of corn (*zea mays*). Sometimes the product remaining after the preparation of alcohol from corn is used, the oil in such a case containing much free acid. The color ranges from yellow to orange and the odor and taste are suggestive of corn. It is a so-called semi-drying oil, resembling cottonseed oil generally, although somewhat different in composition.

The glycerol esters contained in corn oil, as indicated by the acids obtained from the saponified oil, are quite varied in character. Among the acids that have been thus obtained are formic, acetic, stearic, palmitic, arachidic, hypogæic, oleic, linoleic and, according to certain authorities, caproic, caprylic and capric acids. There is some question

whether stearin is always present or not. Hehner and Mitchell were unable to find it in a sample examined by them.

The unsaponified matter is rather high, Vulté and Gibson \* having found 1.4 percent of phytosterol and about 1.1 percent of lecithin. Tolman and Munson found the free fatty acids to range from 1.8 percent to 3.6 percent.

Corn oil is used as an olive oil substitute and adulterant, and in the manufacture of compound lard and oleomargarine.

#### ARACHIS OR PEANUT OIL

This oil, also called earth-nut or ground-nut oil, is obtained by pressure from the tubers (peanuts) of the plant *Arachis hypogaea*, L. Both the first and second pressings are used for salad oils, the former being nearly colorless and the latter a pale greenish-yellow. The oil has a pleasant odor and nutty flavor and is much used in Europe, under its own name. It is used occasionally as an adulterant for olive oil in this country and more frequently so in Europe. It is itself adulterated with sesame, poppy-seed, rape and cottonseed oils. The so-called "peanut-butter" consists simply of ground roasted peanuts.

The solid glycerol esters present in peanut oil are those of arachidic and lignoceric acids (3 to 5 percent) and probably palmitic acid. The liquid esters present are those of oleic, linoleic and hypogæic acids. Tolman and Munson found the free fatty acids to range from 0.24 to 13.51 percent, but Lewkowitsch's maximum limit of 4 percent is probably nearer being normal. The various constants of peanut oil are so little different from olive oil that considerable quantities of it could be mixed with olive oil without being detected by these figures. It is usual to determine the proportion of the mixture of arachidic and lignoceric acids (melting point 72° to 73° C.) present, when adulteration with peanut oil is suspected.

#### SESAME OR GINGILI OIL

This oil, also called Teel oil, is obtained from the seeds of *Sesamum orientale* and *S. indicum* by pressure. It has a yellow color, little or no odor and pleasant taste. Sesame oil is considered by many to be fully equal to olive oil as a salad oil and it is sometimes substituted for or used as an adulterant of that oil. It is itself adulterated with cottonseed, peanut, poppy-seed and rape oils.

\* *J. Am. Chem. Soc.*, 22, 453 (1900); 23, 1 (1901).

The principal glycerol esters to be found in sesame oil are those of palmitic, oleic and linoleic acids, there being considerable of the latter present judging from the "iodine absorption" value. Sesame oil is much used abroad as a compulsory addition to butter substitutes in order to facilitate the detection of these. A very small quantity gives a bright crimson color when shaken with an alcoholic solution of furfural and hydrochloric acid. This is known as the Villavecchia and Fabris test. The free fatty acids in sesame oil range from 0.5 to 6 percent.

#### RAPE OR COLZA OIL

There are several different oils sold under the terms rape or colza oil, the source and composition of which may be considered practically identical. They are obtained from different species of *Brassica* of the *Cruciferae* family and are sometimes used for adulterating olive oil, although their acrid taste, even when refined, renders such practice limited. Fatty mustard oil and radish oil from *Raphanus sativus* may also be classed with this group, their general characteristics differing but slightly from rape or colza oil. The refined rape oil is pale yellow in color with a characteristic odor.

It is composed of the glycerol esters of stearic, oleic and erucic acids, one-half of the latter being in an isomeric form known as "rapic" acid. According to Ponzio \* there is also present about 0.5 percent of glycerol ester of arachidic acid. The solid fat deposited by old oils consists of dierucin, a glycerol ester with two instead of three erucic acid groups introduced into the molecule. The oil also contains about 1 percent of phytosterol and the free fatty acids range from 0.5 to 5 percent. It is occasionally adulterated with radish and fatty mustard oil.

#### SUNFLOWER OIL

The seeds of the sunflower (*Helianthus annuus*) yield an oil by pressure, which is used in Russia and other sections of Europe for culinary purposes. It is also used to adulterate olive oil and, according to Jolles, has been used in the manufacture of oleomargarine. The taste is mild and it has a pleasant odor.

Oleic and linoleic acids are the principal liquid fatty acids, the glycerol esters of which are found in sunflower oil. Tolman and Munson, in two samples, found 0.18 and 1.72 percent of free fatty acids. The various constants are so widely different from those of olive oil,

\* *J. Prakt. Chem.*, 1893, 487.

that a small addition of sunflower oil to olive oil would be sufficient to make the values of the latter abnormal. This is also true of poppy-seed oil.

#### POPPY-SEED OIL

This is obtained by pressure from the seeds of *Papaver somniferum*, and is quite largely used in Europe as a salad oil. It is also used to adulterate olive oil. The taste and odor are pleasant and the oil does not turn rancid upon long standing. The oil from the first pressings is nearly white in color.

The solid glycerol esters present are those of stearic and palmitic acids. Esters of liquid fatty acids in the proportions of 65 parts linoleic acid, 30 parts oleic acid and 5 parts linolenic acid are also present. The free fatty acids range from 0.7 to 3 percent.

#### COCONUT OIL

The product called coconut oil is a semisolid white fat at ordinary temperatures, expressed with the aid of heat from the kernel of the coconut, particularly *Cocos nucifera* and *C. butyracea*. When fresh it has a pleasant taste and odor, suggesting coconut, but it easily becomes rancid. A refined oil is used as a lard substitute under the name "Konut"; and by treatment with steam and other refining processes a white neutral product with good keeping qualities is obtained and used for food purposes under a variety of fanciful names, such as "vegetable butter," "laureol" or "nucoline." A so-called "coconut olein" and "coconut stearine" are obtained by submitting the oil to pressure. Coconut oil is largely used in the manufacture of nut oleomargarines and was used in considerable quantity in the manufacture of "filled" milks, such as "Hebe," etc. Recent absurd legislation stopped the manufacture of this product.

Coconut oil contains about 26 percent of olein; a large proportion of the glycerol esters of myristic and lauric acids; and small quantities of stearin and the glycerol esters of "volatile" acids, caproic, caprylic and capric. Tolman and Munson found 0.11 percent of free acid in a sample examined at the Bureau of Chemistry.

#### PALM OIL

Palm oil is obtained from the fleshy part of the fruit of *Elæis guineensis* by pressure. The color is usually a dark yellow and on this account the oil has been used in the manufacture of oleomargarine,



in order to obtain a color resembling butter, without resorting to the use of forbidden artificial colors. The oil has a sweet taste, with violet-like odor when first expressed.

Palm oil contains a very large proportion of free fatty acid (palmitic principally) even when fresh and upon long standing it may split up completely into free acid. Tolman and Munson found 19.53 percent of free acid in a commercial palm oil examined at the Bureau of Chemistry. In addition to free palmitic acid, palm oil contains palmitin, olein and about one percent of an ester of stearic acid.

#### COCOA-BUTTER

Cocoa-butter, or, as some prefer to call it, "cacao-butter," is the fat obtained by pressure from the beans of *Theobroma cacao*. It is obtained as a commercial by-product of value, in the manufacture of cocoa from cocoa nibs and is used for a variety of purposes, as a food and as a cosmetic. When freed from coloring matter of the cacao-bean it appears as a yellowish-white fat, solid at ordinary temperatures, but quickly melting in the mouth, or when merely rubbed between the fingers. The melting point ranges from 29 to 34° C. It has a pleasant odor and taste somewhat resembling chocolate. Insoluble in 90 percent alcohol, but dissolves in 5 parts of boiling absolute alcohol. Similar to all fats, it is very soluble in ether, petroleum ether and other hydrocarbons.

Cocoa-butter is composed of the glycerol esters of stearic, palmitic and lauric acids principally, there being about 40 percent of the first named acid present. Smaller quantities of the esters of arachidic, linoleic, formic, acetic and butyric acid are to be found.

Cocoa-butter is frequently adulterated and it has also been asserted that other fats are substituted for it in cacao products that should contain the natural proportion of fat, such as chocolate. Tallow, stearic acid, lard, paraffin, beeswax, coconut oil, arachis, sesame, and almond oils and a palm oil product called "copraol" are the principal adulterants. By the determination of certain constants and by several special tests, most of these adulterants are easily detected. Cocoa-butter is sometimes used to harden mixtures of cooking fats.

#### SOY-BEAN OIL

The oil expressed from the soy bean is now a regular article of commerce and is being imported in fairly large quantities from the

Orient. It has been reported as an adulterant of olive and other edible oils, but is an acceptable product, when refined, under its own name.

The glycerol esters present are those of oleic, linoleic, palmitic, stearic, linolenic, and a small proportion of arachidic acid. The unsaponifiable matter in a sample made at the U. S. Bureau of Chemistry was 0.6 percent.

The specific gravity of the oil at 25° C. is about 0.9203 and at the standard temperature of 15.5° C. about 0.9249. The index of refraction ranges from 1.4734 to 1.4741, the iodine absorption ranges from 128.0 to 134.0 and the saponification number ranges from 189.5 to 195.0. The Reichert-Meissl number (0.16) is very low and in the sample made at the Bureau of Chemistry the percent of free fatty acids was low, but in commercial samples, considerable free fatty acid is present, unless the oil has been refined.

Other recent additions to the already long list of edible oils are tomato-seed oil and grape-seed oil, both acceptable food oils.

## Chapter VI.

### The Legal Chemistry of Cacao Products.\*

The legal chemistry of the products of the cacao bean is of considerable interest and is based on the latest Federal standards, which are as follows:

F. I. D. 191

Issued January 19, 1923.

#### UNITED STATES DEPARTMENT OF AGRICULTURE,

OFFICE OF THE SECRETARY.

WASHINGTON, D. C.

#### FOOD INSPECTION DECISION 191.

##### c. Cacao Products.

The following definitions and standards for cacao products were adopted by the Joint Committee on Definitions and Standards, September 29, 1922, and were approved by the Association of American Dairy, Food and Drug Officials, October 5, 1922, and by the Association of Official Agricultural Chemists, November 17, 1922:

1. Cacao Beans, Cocoa Beans, are the seeds of trees belonging to the genus *Theobroma*, especially those of *Theobroma cacao* L., and closely related species.

2. Cacao Nibs, Cocoa Nibs, "Cracked Cocoa," are roasted or dried cacao beans, broken and freed from germ and from shell or husk.

3. Chocolate, Plain Chocolate, Bitter Chocolate, Chocolate Liquor, Chocolate Paste, Bitter Chocolate Coating,† is the solid or plastic mass obtained by grinding cacao nibs and contains not less than fifty percent (50%) of cacao fat and, on the moisture- and fat-free basis, not more than eight percent (8%) of total ash, not more than four-tenths percent (0.4%) of ash insoluble in hydrochloric acid, and not more than seven percent (7%) of crude fiber.

4. Sweet Chocolate, Sweet Chocolate Coating, is chocolate mixed with sugar (sucrose), with or without the addition of cacao butter, spices, or other flavoring materials, and contains, on the moisture-, sugar-, and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

5. Milk Chocolate, Sweet Milk Chocolate, is the product obtained by grinding chocolate with sugar, with the solids of whole milk, or the constituents of milk solids in proportions normal for whole milk, and with or without cacao butter and/or flavoring material. It contains not less than twelve percent (12%) of milk solids.

6. Cocoa, Powdered Cocoa, is chocolate deprived of a portion of its fat and pulverized, and contains, on the moisture- and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

7. "Breakfast Cocoa" is cocoa which contains not less than twenty-two percent (22%) of cacao fat.

\* Originally published in *The Spice Mill*, May, 1923.

† Definition and standards for alkalinized products will form a separate schedule.

8. Sweet Cocoa, Sweetened Cocoa, is cocoa mixed with sugar (sucrose), and contains not more than sixty-five percent (65%) of sugar in the finished product, and, on the moisture-, sugar-, and fat-free basis, no greater percentage of total ash, ash insoluble in hydrochloric acid, or crude fiber, respectively, than is found in moisture- and fat-free chocolate.

9. Sweet Milk Cocoa is the product obtained by grinding cocoa with sugar, with the solids of whole milk, or the constituents of milk solids in proportions normal for whole milk, and with or without flavoring material. It contains not less than twelve percent (12%) of milk solids.

The foregoing definitions and standards are adopted as a guide for the officials of this department in enforcing the Food and Drugs Act.

HENRY C. WALLACE,  
*Secretary of Agriculture.*

Washington, D. C., December 18, 1922.

The concluding statement as to these standards being "adopted as a guide for the officials" of the U. S. Department of Agriculture in "enforcing the Food and Drugs Act" may also be understood to be true as concerns the various State food inspection departments, as the standards themselves are partly the work of the "Association of American Dairy, Food and Drug Officials" and were approved by that association.

The basic standard is the standard No. 3 for Plain Chocolate, (Bitter Chocolate, Chocolate Liquor, Chocolate Paste or Bitter Chocolate Coating), as most of the other products are calculated back to the analytical limits fixed in that standard. This new standard for "Plain Chocolate" is a great improvement over the previous standard, mainly because most of the items are calculated to a moisture-free and fat-free basis, whereas in the old standard direct limits were fixed. Most of all, the old standard fixed a low minimum (45 percent) for cacao-fat and, in judging the purity of powdered cocoa, many analysts took 45 percent as the basis of estimating the proportion of fat removed, instead of the considerably higher figure (52 percent) which represents the *average* fat content of plain chocolate.

The new limit for fat in plain chocolate is 50 percent which represents the reported minimum on samples of known purity. The old 45 percent fat limit was an attempt on the part of food inspection officials to allow for a possible extreme case of a very low natural fat content in cocoa beans, but, like many other liberal *minimum* limits fixed in food standards, it was seized upon by certain trade interests as an invitation to tamper with natural products, to remove some important constituent to as great an extent as the *minimum* standard made legally safe. A classic example is the almost universal robbing of milk down to the minimum fat content fixed in various State and

city standards. A minimum standard is not intended to be a selling standard. It is simply a liberal provision against injustice that might be caused by an unusually low natural value for some food constituent. The selling standard should be the *average* value for the analytical item in question, whether it be the fat of milk or the fat of cocoa beans.

There are many analyses of pure roasted "Cocoa Nibs" ("Cracked Cocoa") in food inspection literature, but the writer has never seen one that justified the old 45 percent fat limit in plain chocolate. The lowest reliable minimum reported was a sample of "Ovello" which showed 48.1 percent fat and a "Selected Venezuelan" with 48.2 percent fat, but the average was 50.1 percent for 19 varieties of beans and in many analyses of reliable brands of plain chocolate (bitter chocolate or chocolate liquor) only once or twice has the fat content been very slightly below 50 percent, while the average was 52.1 percent with a maximum of 54 percent.

As concerns the fiber content of roasted cocoa nibs, most of the published data are on samples which have been hand picked; hence it does not represent actual manufacturing conditions, where the proportion of unremoved shell is noticeably greater, ranging from better grades showing about 1 percent shell to other commercially pure grades showing 2 percent shell. The Federal food inspection experts now regard more than 2 percent shell in plain chocolate as excessive and are perfecting microscopical methods whereby any noticeable excess can be detected.

Meanwhile the best method of judging any excess of shell has been the "crude fiber" value, when figured to a moisture-free and fat-free basis. The new Federal limit for crude fiber in plain chocolate and derived products is 7 percent, on said moisture-free and fat-free basis. There are some recent reliable data on cocoa nibs that suggest that 8 percent crude fiber should be tolerated, but the 7 percent limit mentioned above is usually fair enough. The maximum crude fiber value in the 19 varieties of cocoa nibs referred to above was 3.2 percent and this would be increased to 3.5 percent, by the fiber coming from 2 percent of shell. Then figured to a moisture-free and fat-free basis, as called for in the new standard, we would have but a trifle over 7 percent, as an extreme case.

In the old cocoa standard, the question of the proportion of fat removed was a big and uncertain factor. In the new cocoa standard, it is easily taken care of by referring to a moisture-free and fat-free basis and calling for the same limits as in plain chocolate when re-

ferred to a moisture-free and fat-free basis. In sweet chocolate and sweet cocoa the same limits are referred to, by specifying a moisture-free, fat-free and sugar-free basis of calculation. In milk chocolate (sweet milk chocolate) provision is made for added "cocoa-butter" and flavoring material and at least 12 percent of whole milk solids called for, which may be added as dried whole milk or dried skim milk plus milk-fat in the normal proportion necessary. Added "cocoa-butter" is also allowed in sweet chocolate (sweet chocolate coating).

A "breakfast cocoa" containing at least 22 percent of cocoa-fat ("cocoa-butter") is provided for in the new standards, a limit of 65 per cent sugar in sweetened cocoa is fixed, and a "sweet milk cocoa" provided for, calling for 12 percent milk solids, which may be added as in the case of milk chocolate.

The limits for "total ash" and "acid-insoluble ash" fixed in the standard for plain chocolate, and referred back to in the various derived products, are for the purpose of controlling the cleanliness of the raw materials. Any sand or clay will increase the acid-insoluble ash and mineral dirt of any kind will increase the total ash. The old standard fixed a limit for starch, but as no added starchy matter is permitted in pure cocoa products, there is no need of fixing a limit on the cocoa starch naturally present.

The following data on many various pure cocoa products will give an idea of their natural range of composition. See Table 54.

In regard to cocoas which have been treated with alkalis (usually potassium carbonate), the Federal inspection chemists have studied the question somewhat extensively (see Bulletin 666 of the U. S. Department of Agriculture) but no standard was decided upon therein. Service and Regulatory Announcement No. 28 of the U. S. Bureau of Chemistry says: "Cocoa treated with an alkali or an alkaline salt, as in the so-called 'Dutch Process' should be labeled with a statement of the presence of added mineral ingredients. Cocoa is not soluble, and when so treated shows essentially the same lack of solubility. It is, therefore, improper to describe alkali-treated cocoa as 'soluble.' The word 'instant,' which may be construed to imply solubility, is subject to the same objection."

Very recently the Federal definition and standard for alkali-treated cacao products has been fixed as follows: "Dutch-Process Chocolate," "Alkalized Chocolate" and Dutch Process Cocoa, "Alkalized Cocoa," are modifications, respectively, of chocolate and cocoa, in that, in their manufacture, an alkali carbonate, or other suitable alkaline substance, has been employed. In the preparation of these products, not more

Table 54. Composition of Cacao Products.

	Percent								
	Roasted Whole Beans	Roasted Nibs	Plain Chocolate	Cocoa	Shells	Sweet Chocolate	Sweet Cocoa	Milk Chocolate	Milk Cocoa
Moisture (minimum)	2.50	2.19	3.18	2.00	3.71	1.82	1.68	0.70	2.48
" (maximum)	3.50	3.21	4.60	8.90	6.57	2.95	3.87	3.25	3.70
" (average)	2.96	2.80	3.82	5.90	4.87	2.18	2.90	1.90	3.20
Cocoa-fat (minimum)	41.80	48.11	49.96	12.37	1.66	19.31	5.31	18.30	5.12
" (maximum)	48.78	58.06	54.05	37.22	5.30	41.20	29.64	32.72	16.02
" (average)	44.71	53.12	52.10	26.72	3.60	29.50	14.10	27.05	10.50
Crude fiber (minimum)	3.62	2.20	2.64	3.18	12.43	0.72	1.92	0.67	1.80
" (maximum)	5.20	3.52	3.85	5.37	19.21	1.53	4.76	0.81	4.35
" (average)	4.32	2.70	2.90	4.40	16.63	0.98	3.20	0.75	3.10
Total ash (minimum)	3.20	2.61	2.80	3.72	7.14	0.96	2.71	1.84	2.67
" (maximum)	5.82	4.15	3.74	5.85	16.66	2.00	4.63	2.49	4.80
" (average)	4.16	3.35	3.20	5.32	10.40	1.40	2.95	2.02	3.15
Acid-insol. ash (minimum)	0.03	0.00	0.02	0.01	0.05	0.00	0.08	0.08	0.06
" " (average)	1.61	0.15	0.18	0.34	7.02	0.13	0.39	0.23	0.30
" " (maximum)	0.33	0.06	0.07	0.22	2.45	0.05	0.20	0.10	0.17
Alkaloids (minimum)	1.15	1.20	0.82	1.03	0.30	0.37	0.45	0.33	0.33
" (maximum)	1.50	1.62	1.09	1.67	0.94	0.57	0.73	0.36	0.36
" (average)	1.32	1.44	0.94	1.31	0.65	0.43	0.59	0.34	0.34
Starch (minimum)	6.26	6.19	7.47	8.69	3.36	2.11	3.45	2.36	2.36
" (maximum)	8.44	8.99	8.88	13.46	5.16	4.02	6.65	2.75	2.75
" (average)	7.86	8.07	8.11	11.14	4.14	2.88	5.25	2.50	2.50
Protein (minimum)	11.44	11.00	12.00	15.18	10.69	3.31	7.31	7.50	7.50
" (maximum)	13.21	13.06	12.87	19.37	18.06	5.81	9.25	11.97	11.97
" (average)	12.35	12.12	12.36	18.34	14.54	4.58	8.36	8.40	8.40
Sugar (minimum)	none	none	none	none	traces	30.80	26.96	36.08	26.96
" (maximum)	traces	traces	none	traces	3.50	63.88	57.86	44.89	44.89
" (average)	.....	.....	.....	.....	.....	50.15	42.15	40.25	40.25
Milk-fat (minimum)	.....	.....	.....	.....	.....	.....	.....	3.26	3.40
" (maximum)	.....	.....	.....	.....	.....	.....	.....	7.00	9.48
" (average)	.....	.....	.....	.....	.....	.....	.....	4.30	4.30
Milk-solids (minimum)	.....	.....	.....	.....	.....	.....	.....	11.37	12.15
" (maximum)	.....	.....	.....	.....	.....	.....	.....	21.60	18.20
" (average)	.....	.....	.....	.....	.....	.....	.....	17.25	15.80

## On Moisture-Free, Fat-Free and Sugar-Free Basis

Crude fiber (minimum)	6.94	4.70	5.22	4.62	13.71	3.40	5.92	.....	.....
" (maximum)	9.42	7.09*	6.98*	7.20	7.45	6.70	7.45	.....	.....
" (average)	8.18	5.70*	5.88*	6.15	18.01	5.95	6.20	.....	.....
Total ash (minimum)	6.39	5.76	5.70	6.02	5.63	5.00	6.27	.....	.....
" (maximum)	11.08	8.81	7.95	8.95	17.79	8.40	9.34	.....	.....
" (average)	8.02	7.04	6.80	7.08	11.30	6.95	8.01	.....	.....
Acid-insol. ash (minimum)	0.06	0.00	0.04	0.05	0.06	0.00	0.25	.....	.....
" (maximum)	3.04	0.35	0.36	0.42	7.50	0.36	0.36	.....	.....
" (average)	0.62	0.12	0.15	0.21	2.70	0.19	0.30	.....	.....

\* More recently Taber and Offutt of the U. S. Bureau of Chemistry have reported on thirty samples of shelled beans in common use at the present time, especially Accra, Bahia, Trinidad and Maracaibo, and report 9.83 percent as a maximum, with an average of 7.21 percent See *Journal A. O. A. C.*, Vol. VII, No. 2, p. 148.

than three parts by weight of potassium carbonate, or the neutralizing equivalent thereof in other alkaline substance, are added to each 100 parts by weight of cacao nibs. The finished products conform to the standards for chocolate and cocoa, respectively, due allowance being made for the kind and amount of alkaline substance added."

The concluding statement in the investigation mentioned above (Bulletin 666, U. S. Dept. Agriculture) was "that the claim that the alkali treatment increases the amount of cocoa soluble in water is absolutely without foundation."

The effects that were observed were an increase in the color of the water infusion of the cocoa, an increase in the total ash and the water-soluble ash and (on the average) more than a doubling of the alkalinity of the water-soluble ash, ranging (on a moisture-free and fat-free basis) from 2.25 cc. to 11.15 cc. (average 5.46 cc.) of tenth-normal acid per one gram of sample, whereas untreated cocoa ranged from 1.8 cc. to 3.05 cc., averaging 2.30 cc.

When ammonium carbonate alone was used for treating the cocoa, there was no decided increase in total ash, water-soluble ash or alkalinity of ash, but there was a distinct increase in the nitrogen content of the cocoa, due to ammonia remaining in the cocoa.

The alkali treatment, however, does produce a cocoa which forms a more perfect suspension in the cup, due largely to the fact that during the treatment some of the cocoa starch is gelatinized. Possibly traces of soap are formed by action of alkali on fat and this would assist in forming an emulsion and better suspension of cocoa constituents.



## Chapter VII.

### The Legal Chemistry of Spices.\*

Under the general heading, "Condiments (Except Vinegar and Salt)," spices are defined in the Federal standards of purity for food products as "aromatic vegetable substances used for the seasoning of food and from which no portion of any volatile oil or other flavoring principle has been removed, and which are clean, sound and true to name."

At first thought it would seem as though the above general specification as to what constitutes a legally pure spice was a sufficiently exact standard in itself. Owing, however, to a number of confusing differences in trade ideas and practices regarding certain similarly-named, but botanically and condimentally different spices, it has been considered desirable by the food standard commission to specifically define each and every commonly known spice, stating particularly the botanical species or genus derived from, and the portion (including the condition, i.e., dried, immature, etc.) of the same to be used.

On account also of the widely varying degrees of knowledge, ideas, and honestly or unscrupulously held opinions among chemists (even food chemists sometimes) as to what is normal and what is abnormal when interpreting a spice analysis, it has been considered desirable by the food standard commission to fix, as far as practicable, certain analytical limits, for example, the maximum proportion of ash, or mineral matter, natural and not too far removed from the normal, for the spice in question.†

The data available for this purpose were not always as extensive or reliable as was desirable, and in a few cases the limits fixed or called for in the Federal standards must be considered as practically tentative and subject to revision when the reason for the same is properly and sufficiently demonstrated, privately or in court.

Generally speaking, however, the analytical limits fixed for spices

\* Published originally in *The Spice Mill*.

† The standards fixed are such that a departure of the articles to which they apply, above the maximum or below the minimum limit prescribed, is considered evidence that such articles are of inferior or abnormal quality, or, legally speaking, adulterated. (Circular 19, page 4.)

in the Federal standards are very fair and liberal almost to an excess. This liberality results from the necessity of passing as legally pure even the very lowest quality of a naturally normal, pure spice. As expressed to the author by a prominent spice grinder recently, this liberality will enable, in the cases of those who find competition very sharp or the pressure of the law unfair or too severe, considerable hygienically harmless sophistication without any provable transgression of the legal analytical limits. It is to be hoped, of course, that this method of evasion will not be considered necessary or resorted to in actual trade practice.

#### ALLSPICE OR PIMENTO

The first of the spices classified, defined, etc., in the Federal standards is allspice or pimento, and is, at present writing, standardized as follows: "Allspice, pimento, is the dried, nearly ripe fruit of *Pimenta officinalis* (L.) Karst, and contains not less than eight (8) percent of quercitannic acid (calculated from the total oxygen absorbed by the aqueous extract); not more than six (6) percent of total ash, not more than four-tenths (0.4) percent of ash insoluble in hydrochloric acid; and not more than twenty-five (25) percent of crude fiber." \*

Regarding the appearance, geographical sources, quality, variations, etc., of allspice, the readers of this section are assumed to be informed. A cross-section of an allspice or pimento berry shows an exterior pericarp or woody skin inclosing a two-celled cavity with a single brown seed in each, covered with a thin outer coating inclosing a spiral-like embryo. The berries are gathered before fully ripe, as some of the aroma is lost if they are allowed to mature completely.

In chemical composition allspice most closely resembles cloves, particularly the so-called "mother cloves," or clove fruit. It contains from 3 to 4.5 percent of a volatile oil, very similar in chemical constitution to clove oil; and, similarly to cloves, a fairly large and constant proportion of tannin (quercitannic acid). Unlike cloves, but like "mother cloves," allspice contains starch, the latter appearing under the microscope as small, nearly circular granules, usually showing a central spot or hilum and often arranged in groups like buckwheat starch granules.

Estimated as true starch by the diastase method, Winton *et al.* report only from 1.8 to 3.8 percent, but judging from the copper

\* The National Formulary or drug law standard calls for not over 5 percent of stems or other foreign matter, crude fiber not over 25 percent, total ash not over 6 percent.

reducing value resulting upon heating with acid, calculated as starch (which ranges from 16.5 to 20.6 percent) it is evident that considerable gum or pentosan-like material closely related chemically to starch exists in allspice. A proximate analysis (Table 55), showing the variations in composition as reported in twenty-five analyses of pure allspice, has been compiled by the writer.

Table 55. Allspice Analyses.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	5.51	10.14
Ash (mineral residue) .....	4.01	7.51
Ash insoluble in acid .....	0.00	0.95
Volatile ether extract (oil) .....	1.29	5.21
Non-volatile ether extract .....	1.60	7.72
Starch (by diastase method) .....	1.82	3.76
Copper reducing value as starch .....	16.56	20.65
Crude fiber .....	13.45	23.98
Protein (Nitrogen x 6.25) .....	4.03	6.37
Quercitannic acid .....	4.32	12.48

It will be immediately noticed by the reader that among the above figures there are several which transgress the limits fixed in the Federal standards, particularly the minimum value for quercitannic acid (reported by Richardson, former chief of the Bureau—then Division—of Chemistry at Washington) and the maximum figures for total and acid-insoluble ash. This acid-insoluble ash, by the way, is generally considered and often reported as "sand," and any undue proportion of sandy, gritty matter mixed with the pimento berries is indicated by this analytical item.

The guiding principle whereby the food standard commission feels justified in fixing limits which rule out such data is given in the preface to the original standards (Circular 19, U. S. Dept. of Agriculture) as follows: "The limits fixed as standard are not necessarily the extreme authentically recorded for the article in question, because such extremes are commonly due to abnormal conditions of production and are usually accompanied by marks of inferiority or abnormality readily perceived by the producer or manufacturer." Yet it is also stated as a guiding principle that the "standards are based on data representing materials produced under American conditions and manufactured by American processes or representing such varieties of foreign articles as are chiefly imported for American use."

If, therefore, it appears to the conscientious spice grinder or broker that one or more Federal standards are unfair, viewed from the standpoint of the above "principle," it would seem that it was up to him

to demonstrate with sufficient, carefully determined, bonafide data the point in question, to the food standard commission, who in turn is thus forced to investigate the subject further and correct the unfairness, if such.

The crude fiber limit in the Federal standard for allspice appears liberal enough to cover any true case, and probably only an exceptional sample would show much below 8 percent in quercitannic acid. Many more data, however, on the last point are needed, together with data on the total ash content.

It must not be supposed that any mixture of allspice and one or more adulterants which does not in any way overstep the Federal analytical limits for allspice will be passed as legally pure. The definition part of the standard, in fact the name itself, constitutes or implies a certain natural, normal make-up, and in the hands of a trained food microscopist the adulteration will be detected and the sample condemned, in spite of compliance with the analytical limits. The microscope, in fact, is an absolutely indispensable auxiliary in spice analysis; often the microscopical examination is the only mode of analysis necessary and capable of showing the exact nature of the adulterant, as required in a court case.

#### ANISE, CARAWAY, CARDAMON AND CAYENNE (RED PEPPER)

Included in the Federal standards of purity for food products (Circular No. 136, U. S. Dept. of Agriculture) are a number of somewhat uncommon condimental substances classed as spices, only a few of which can be purchased in the usual grocery store, and nearly all of which are sold in an unground condition. In taking up the various legally defined spices in alphabetical order the next few coming to our attention belong to the above variety, i.e.: Anise,\* "the fruit of *Pimpinella anisum*, L."; Bay leaf, "the dried leaf of *Laurus nobilis*, L."; Capers, "the flower buds of *Capparis spinosa*, L."; Caraway, "the dried fruit of *Carum carvi*, L." containing not over 3 percent of harmless foreign matter, not over 8 percent of total ash nor more than 1.5 percent of ash insoluble in hydrochloric acid; and Cardamon, containing not over 8 percent total ash, nor more than 3 percent of ash insoluble in hydrochloric acid.†

\* Now standardized as containing not over 3 percent of foreign matter, nor more than 9 percent (9%) of total ash, nor more than 1.5 percent of ash insoluble in hydrochloric acid. Total ether extract has been reported as from 21.6 to 26.2 percent.

† A Federal Service and Regulatory Announcement (Item 71) specifies that cardamon must show at least 64 percent sound seed (i.e., pods, etc., not over 36 percent).

The next important spice defined and standardized in the Federal spice standards is cayenne. Taken up in conjunction with the same is paprika; and prefacing both is the definition that "Red pepper is the red, dried, ripe fruit of any species of *Capsicum*," containing not over 8 percent total ash, nor more than 1 percent of acid-insoluble ash.

As officially defined in the Federal spice standards, "Cayenne pepper, cayenne, is the dried, ripe fruit of *Capsicum frutescens*, L., *Capsicum baccatum*, L., or some other small-fruited species of *Capsicum*, and contains not less than fifteen (15) percent of non-volatile ether extract; not more than eight (8) percent of total ash; not more than one and one-quarter (1.25) percent of ash insoluble in hydrochloric acid; not more than one and five-tenths (1.5) percent of starch, and not more than twenty-eight (28) percent of crude fiber." The U. S. P. standard limits stems, etc., to 2 percent and total ash to 7 percent.

Paprika is the dried, ripe fruit of *Capsicum annuum*, L. (see page 184).

The fruit of the capsicum plant is of an elongated, conical form, the surface of which when fresh is smooth and very red. Upon drying, it becomes shriveled and loses some of its brilliant coloring. The pericarp, or shell, is thin and tough and the fruit pod is divided into several cells inclosing many yellow, kidney-shaped seeds. Cayenne contains considerable fixed or fatty oil which, together with certain non-volatile resins, constitutes the analytical item known as non-volatile ether extract; in other words, that portion of cayenne which is dissolved by ether but is not volatilized by continued heating at the boiling point of water or even 10 degrees above. The Federal requirement of 15 percent for this analytical item is evidently very fair, there being no authentic instances of a pure cayenne falling below this figure. The average of twenty-three samples examined in Connecticut showed about 20 percent non-volatile ether extract.

Most of the pungency of cayenne is due to an alkaloid-like crystalline compound known as capsin. It is present in both seeds and pod, but is by far more abundant in the placenta. The volatile portion of the ether extract is made up in part of capsin.

Cayenne contains no true starch, but does contain a slight proportion (about 1 percent) of a dextrin or gum-like substance which, like starch, is converted into sugar by the action of the ferment diastase and in analysis appears as starch. Hence the Federal limit of 1.5 percent "starch." Foreign starches, if present, would be immediately apparent under the microscope, as the granules of pure starch

from various cereals and other starch-containing substances (pepper or horseradish, for instance) are very characteristic in appearance under a powerful magnification.

Table 56 gives the maxima and minima of the analytical results on sixty-eight samples of cayenne or "chillies." \*

Table 56. Cayenne Analyses.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	3.67	7.08
Non-volatile ether extract .....	15.59	23.21
Volatile ether extract .....	0.23	2.57
"Starch" (by diastase method) .....	0.80	1.46
Crude fiber .....	20.35	27.91
"Protein" (N x 6.25) .....	13.31	14.63
Total ash .....	5.08	8.18
Ash insoluble in acid .....	0.05	1.23

The crude fiber (an analytical item comprehending mainly the woody fiber or cellulose of a spice) limit of 28 percent in the Federal cayenne standard is quite liberal. This item in any spice analysis, however, is meaningless for Federal standard comparison purposes unless determined *exactly* as specified in the official testing methods, called for in the Federal food law regulations. Therefore this item may be sometimes reported as exceeding the Federal limit when in reality it would not if the proper testing method had been used by one familiar with official analytical work.

The term "protein" includes all nitrogen-containing compounds in the spice—proteins, amids, alkaloids, etc.—and is utterly without scientific significance, although sometimes useful as an analytical guide. It is determined by estimating the total nitrogen in the substance and multiplying by the factor 6.25.

Some later data reported by Boyles in *Journal of Industrial & Engineering Chemistry*, Mar., 1917, suggest that the standard for non-volatile ether extract should be lowered to 13 percent, and that for crude fiber raised to 30 percent. He reports as high as 32.3 percent crude fiber on a commercially acceptable Bombay capsicum and nearly 30 percent on a "Cherry" type capsicum of highest grade. A type of capsicum grown in South Carolina, from a mild paprika seed, has developed into a very "hot" variety, suitable to be ground as cayenne. The maximum for non-volatile ether extract was only 15.7 percent, the minimum was 10.75 percent, and the average for 17 samples was only 13.92 percent.

\* For data on different varieties, especially African and Japanese, see Bulletin 163 of the U. S. Bureau of Chemistry.

Owing to a pronounced public demand for a bright red paprika, that spice has been found colored with coal-tar colors in the import inspection work, and a number of shipments have been refused entrance at the local port on that account. More often a small percentage of olive oil or other fatty oil is added to improve the color of low grade paprika. Cayenne is sometimes artificially colored also. As adulterants, ground redwood, sandalwood, nut shells, olive stones, ginger, cereal products and gypsum have been reported. Microscopical examination will demonstrate all but the latter, which would be shown by the ash content. The U. S. Department of Agriculture allows 2 percent stems in small capsicums (African chillies) and 5 percent in large (Bombay, Talay, Indian) chillies and Cherries. In any variety not over 10 percent of moldy or wormy pods is tolerated.

#### PAPRIKA AND PIMENTON

Paprika, as defined in connection with the other red peppers, is the dried, ripe fruit of *Capsicum annuum*, L. and, according to the Federal standard in Circular 136 of the U. S. Dept. of Agriculture, should contain "not more than eight and five-tenths percent (8.5%) of total ash, nor more than one per cent (1%) of ash insoluble in hydrochloric acid; and the iodine number of its extracted oil is not less than 125 nor more than 136." "Hungarian paprika" is "paprika having the pungency and flavor characteristic of that grown in Hungary."

Under "Hungarian paprika" we have standardized: (a) "Rosenpaprika, rozsapaprika, rose paprika" as "Hungarian paprika prepared by grinding specially selected pods of paprika, from which the placenta, stalks and stems have been removed. It contains no more seeds than the normal pods, not more than eighteen percent (18%) non-volatile ether extract, not more than twenty-three percent (23%) of crude fiber, not more than six percent (6%) of total ash, nor more than four-tenths percent (0.4%) of ash insoluble in hydrochloric acid." (b) "Koenigspaprika, king's paprika, is Hungarian paprika prepared by grinding whole pods of paprika without selection, and includes the seeds and stems naturally occurring with the pods. It contains not more than eighteen percent (18%) of non-volatile ether extract, not more than twenty-three percent (23%) of crude fiber, not more than six and five-tenths percent (6.5%) of total ash, nor more than five-tenths percent (0.5%) of ash insoluble in hydrochloric acid."

In Bulletin 163 of the U. S. Bureau of Chemistry, entitled the "Composition of Different Varieties of Red Peppers" there are given many data on different combinations of the different parts of the Hungarian paprika pod (and also of the Spanish paprika or pimenton) which we abstract here. The proportions of different parts of the Hungarian paprika pod are as shown in Table 57.

Table 57. Hungarian Paprika Pods.

	Minimum	Percent Maximum	Average
Shell .....	50.5	63.7	56.4
Seeds and placenta .....	28.1	43.2	36.1
Stems .....	6.0	9.4	7.5

When these various parts are combined in different ways and ground the results in Table 58 are obtained. Sixty-eight samples are represented. (See next page.)

It will be seen from this data that the standards for the different grades of Hungarian paprika are very liberal. Only the use of an abnormal proportion of seeds could bring the non-volatile ether extract (fatty oil) above the limit specified, i.e., 18 per cent and only an excess of stems would bring the crude fiber above the 23 percent limit. It is interesting to note, however, that a paprika made by grinding shell only would perhaps exceed the 23 percent limit for crude fiber. It is in the shell and the part of the placenta nearest the shell that most of the flavor, pungency and color is located.

Pimenton (Spanish Paprika), also called "pimienton," is defined in the Federal standards (Circular 136, U. S. Dept. Agr.) as "paprika having the characteristics of that grown in Spain. It contains not more than eighteen percent (18%) of non-volatile ether extract, not more than twenty-one percent (21%) of crude fiber, not more than eight and five-tenths percent (8.5%) of total ash, nor more than one percent (1%) of ash insoluble in hydrochloric acid."

It is a large-fruited pepper, a variety of *Capsicum annum*, L., grown in Spain. The flavor is distinctly different from that of Hungarian paprika and is very slightly pungent. It is imported into the United States largely on account of its coloring value and is used considerably to improve the color of tomato catsup, being a legitimate ingredient of catsup by virtue of its standing as a spice.

The principal sophistication to which it is subject is the addition of a small percentage of some foreign fatty oil, usually olive oil, for the purpose of improving the red color of a sample of poor quality. Inasmuch as the spice is sold mainly on the basis of color, it is held,



Table 58. Ground Hungarian Paprikas.

	Moisture	Volatile Ether Ext.	Non-volatile Ether Ext.	Crude Fiber	"Protein" (N $\times$ 6.25)	Carbo- hydrate (as "Starch")	Total Ash	Acid Insoluble Ash	Water Soluble Ash	Ether Extract (Seeker Method)	Iodine No. of Seeker Ether Extract	Refractive Index of Seeker Ether Extract
Percent												
Shell, seed, placentæ and stems												
Minimum	3.29	0.08	7.42	15.10	14.06	19.56	5.08	0.05	4.67	10.86	129.8	1.4758
Maximum	8.14	1.25	16.43	22.76	17.44	21.40	7.06	0.33	5.68	15.00	137.0	1.4854
Average	5.10	0.59	12.10	19.50	15.70	20.50	5.90	0.22	5.20	12.61	132.6	1.4806
Shell, seeds and placentæ												
Minimum	3.11	0.07	13.94	20.47			4.66	0.20		12.64	129.0	1.4756
Maximum	4.16	0.90	17.35	23.18			5.56	0.31		15.08	133.2	1.4834
Average	3.51	0.34	15.28	21.56			5.22	0.26		13.91	131.9	1.4799
Shell alone												
Minimum	3.44	0.16	4.01	16.66	12.50	22.16	5.50	0.03	4.85	4.14	130.2	
Maximum	9.76	1.10	6.90	24.07	15.37	24.52	7.11	0.37	6.10	5.26	149.5	
Average	6.50	0.51	5.70	21.70	14.05	23.30	6.40	0.17	5.45	4.68	137.0	
Seeds and placentæ												
Minimum	3.73	0.00	17.66	17.29	16.56	17.36	3.06	0.05	1.72	22.53	130.2	1.4691
Maximum	4.56	1.90	27.56	21.60	21.19	18.16	4.93	0.30	3.72	24.96	134.0	1.4699
Average	4.15	0.70	23.50	19.80	18.90	17.76	3.75	0.16	2.70	23.53	133.5	1.4696
Stems only												
Minimum	2.83	0.15	1.38	19.86	14.37		9.84	0.30	6.93		15.3	
Maximum	8.80	0.78	3.05	32.86	18.00		12.25	1.20	9.28		17.0	
Average	5.50	0.37	2.21	29.80	16.20		10.80	0.65	8.10		15.9	

in food inspection circles, that this apparent improvement in the red color is fraudulent, by making the product appear better than it is.

The proportions of shell, seeds and placenta, and stems, in Spanish paprika, or pimenton, have practically the same range and averages as those parts in Hungarian paprika. Table 59 represents seventy samples reported by the U. S. Bureau of Chemistry (Bulletin 163) and other analysts. (See next page.)

By a study of the data of Table 59 it will be seen that the Federal standard limits for non-volatile ether extract (fatty oil) and crude fiber on the whole pod, with or without stems, are entirely liberal enough. Only an excess of stems, or seeds and placenta, might cause crude fiber to run high and only great excess of seeds and placenta or some added oil (for improving color) would cause the limit for non-volatile ether extract (fatty oil) to be exceeded. In fact, for judging if foreign fatty oil is present the official analyst does not confine himself to ascertaining if the 18 percent non-volatile ether extract limit has been exceeded. It is considered that if the maximum values reported below for whole pods (with or without stems), viz.: 13.8 percent and 13.3 percent, especially the former, is noticeably exceeded, either some foreign fatty oil has been added or an excess of seeds is present. If it is the latter the crude fiber will also probably be above the average, but the iodine number of the ether extract (by Seeker's method) will be only slightly below the values as given for the whole pod (with or without stems) or the shell alone.

If the percentage of non-volatile ether extract (by either method) is suspiciously high and the iodine number, or the refractive index, of the Seeker method extract is abnormal, then it is judged that foreign fatty oil is present. Olive oil is most generally used and as the iodine number of olive oil is generally between 80 and 90, averaging 85 or less, it will be seen that even three or four percent of added olive oil will cause a decided lowering of the iodine number of the fatty oil extracted from the paprika sample. Possibly a very small addition of olive oil to a paprika with a Seeker extract iodine number at the maximum would not give an iodine number less than the 125 specified in the general standard for paprika, but this would not pass the sample if the percentage of non-volatile ether extract (either method) was unduly high. Moreover, the refractive index of the Seeker ether extract would probably be suspiciously lowered also.

There are other foreign fatty oils having iodine numbers as high

Table 59. Ground Spanish Paprikas (Pimentons).

	Percent												
	Moisture	Volatile		Non-volatile	Crude	"Protein"	Carbo-	Total	Acid	Water	Ether	Iodine	Refractive
		Ether	Est.	Ether	Fiber	(N x 6.25)	hydrate	Ash	Insoluble	Soluble	Extract	Seeker	Index of
						"Starch")	(as		Ash	Ash	(Seeker	Ether	Ether
							"Starch")				Method)	Extract	Extract
Shell, seeds, placentæ and stems													
Minimum	4.31	0.10	10.05	14.75	14.62	16.52	16.52	5.24	0.05	4.25	9.81	134.5	1.4776
Maximum	8.60	1.18	13.87	20.59	16.87	20.50	20.50	7.86	0.68	6.70	10.81	137.3	1.4818
Average	6.15	0.85	11.20	19.10	15.75	18.60	18.60	7.10	0.35	5.30	10.34	136.2	1.4805
Shell, seeds and placentæ													
Minimum	4.52	0.25	11.58	18.76	11.64	19.96	19.96	6.60	0.24		9.80	134.5	1.4792
Maximum	5.09	0.60	13.34	20.34	14.06	21.90	21.90	7.35	0.40		11.30	137.2	1.4810
Average	4.83	0.44	12.47	19.49	13.05	20.91	20.91	6.98	0.32		10.67	136.1	1.4801
Shell alone													
Minimum	4.74	0.40	4.48	14.80	11.64	19.96	19.96	6.23	0.10	5.70	4.26	130.7	1.4958
Maximum	8.95	1.40	11.00	18.70	14.06	21.90	21.90	8.46	0.37	6.40	4.67	143.7	1.4968
Average	5.70	0.75	6.30	16.30	13.05	20.91	20.91	7.50	0.23	6.20	4.46	136.0	1.4963
Seeds and placentæ													
Minimum	3.59	0.05	18.99	19.48	15.50	16.12	16.12	3.41	0.06	2.23	19.11	128.1	1.4695
Maximum	4.33	2.25	24.58	24.08	16.25	20.10	20.10	5.20	0.31	4.35	21.35	133.3	1.4702
Average	3.90	1.00	22.10	22.10	15.92	18.02	18.02	4.60	0.17	3.37	19.99	131.0	1.4699
Stems only													
Minimum	3.44	0.15	0.98	27.66	11.56			13.00	0.26	11.07		14.9	
Maximum	6.03	0.49	2.05	30.98	15.60			15.77	1.07	13.09		17.0	
Average	5.00	0.31	1.38	29.33	13.70			14.53	0.63	12.00		15.9	

and even higher than that of the fatty oil (Seeker ether extract) from paprika (viz.: poppy-seed oil, 130 to 141; sunflower seed oil, 119 to 135; soy bean oil, 128 to 134, and linseed oil, 171 to 181), but with even these oils it would be necessary to know that the paprika ran low in fatty oil and not to add enough of the foreign oil to exceed the whole pod maximum of 13.8 percent mentioned above. All these oils would also have a tendency to lower the refractive index of the Seeker extract, although perhaps not conclusively.

Lowenstein and Dunne, in the April, 1910, issue of the *Journal of Industrial and Engineering Chemistry*, report on various paprikas of somewhat doubtful quality (possibly old and oxidized) and give an iodine number as low as 113.3 on fatty oil from whole Spanish pods, that, judging from the value for non-volatile ether extract (12.76%), contained no added foreign fatty oil. On a sample of shell alone they similarly report an iodine number of 114.8 and on seeds and placenta, obviously containing no added fatty oil, they give iodine numbers as low as 110.1 and 113.9.

However, these iodine numbers were determined on the regular non-volatile ether extract, which is so treated and heated (during drying) as to probably oxidize and alter the constants (especially the iodine number) of the fatty oil.

The Seeker method of extracting and quickly drying the fatty oil of the paprika avoids the above possibilities and it is very probable that if Lowenstein and Dunne had used this newer method, such low values for iodine number (on evidently legally pure samples) would not have been obtained.

An excess of seeds and placenta will raise the non-volatile ether extract and lower the iodine number a trifle, but this is, in itself, an adulteration as reprehensible as adding foreign fatty oil, if not more so.

It will be seen that none of the reported samples of whole pods (with or without stems) or shell alone exceeded the Federal standard limits for total ash or ash insoluble in acid and only when pods are allowed to dry on the earth and are spattered with dust and sand (by rain, etc.) will the limit prescribed be exceeded.

The Spanish paprikas (pimentons) have little or no pungency and are used more for coloring value (in tomato catsup for instance) than spice value. The fresh pod is used extensively for stuffing olives and when canned fresh they make a nice addition to salads and are used in making pimiento cream cheese.

## CELERY SEED

Next in order to cayenne and paprika, comes celery seed, legally defined in the Federal food standards as the "dried fruit of *Apium graveolens*, L., containing not more than 10 percent (10%) total ash nor more than 2 percent (2%) ash insoluble in hydrochloric acid." For import it must be 95 percent sound seed. Volatile oil should be not less than 2 percent.

## CINNAMON AND CASSIA

Cinnamon is now so defined legally as to include cassia, being stated to be "the dried bark of cultivated varieties of the genus *Cinnamomum*, from which the outer layers may or may not have been removed." "True cinnamon," by which is meant the thin, closely rolled inner bark from the tree native to Ceylon, is defined in the Federal standards as "the dried bark of cultivated varieties of *Cinnamomum zeylanicum*, Breyne." The yield of true cinnamon is very small and very little of it reaches this country.

True cinnamon is of a pale, yellow-brown color, the outer surface of the quill-like roll being marked with round, dark spots and furrowed longitudinally with wavy, light-colored lines. Its thickness varies from 1 to 3 millimeters.

The odor of cinnamon is due to a volatile oil, of which from 1 to 3 percent is present; and which is composed principally of cinnamic aldehyde and eugenol, at least 65 percent of the former and not more than 10 percent of the latter being required in the Federal standard for oil of cinnamon. It is very pungent and sweet and constitutes almost entirely the analytical item called "volatile ether extract." Starch is present in cinnamon (from 15 to 25%) as circular, microscopical granules, considerably resembling allspice starch granules, and like the latter, ranging from 8 to 12 microns in diameter. Cinnamon contains a little tannin, some gum,\* and naturally, a large proportion of woody fiber (cellulose, etc.) included under the analytical item "crude fiber."

The results of twelve analyses of "true cinnamon" compiled by the writer are shown in Table 60. (See next page.)

Cassia, Saigon cinnamon, is defined in the Federal standards as "the dried bark of cultivated varieties of *Cinnamomum cassia*."

\* Hanus and Bien (*Z. Nahr. Genussm.*, 12, 395) report pentosans in 39 spices. In cinnamon they report 8 percent mannite and araban, galactan and xylan (also glucosan).

Table 60. Analyses of True Cinnamon.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	5.40	12.44
Volatile ether extract .....	0.72	3.14
Non-volatile ether extract .....	1.35	3.30
Crude fiber .....	25.63	38.48
Starch (by acid method) .....	16.65	22.00
"Protein" (N x 6.25) .....	2.98	4.06
Total ash (mineral residue) .....	3.40	5.99
Ash insoluble in acid ("sand") .....	0.02	0.58

Cassia buds were defined as "the dried, immature fruit of species of *Cinnamomum*."

The cheaper and most common cassia is the dried bark of *Cinnamomum cassia*, coming from China, India and Indo-China. It is darker in color and coarser in texture than "true cinnamon," and from three to four times as thick. The outer surface of the roll is marked with warty protuberances and does not have the wavy lines characteristic of "true cinnamon."

Cassia buds are found in the market both in whole and in powdered form, and are often contained in the cheaper grades of ground cassia. Cassia contains a volatile oil very similar to that found in "true cinnamon," but containing at least 75 percent of cinnamic aldehyde, according to the Federal standards. Starch is a little more abundant in cassia than in cinnamon, and the circular granules of it are a trifle larger, ranging from 13 to 23 microns in diameter. Cassia buds are similar in composition to cassia bark, containing, however, less starch and fiber and more volatile oil.

Table 61 gives the results of twenty-six analyses of cassia, compiled by the writer.

Table 61. Cassia Analyses.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	6.53	17.45
Volatile ether extract .....	0.55	5.15
Non-volatile ether extract .....	0.74	4.13
Crude fiber .....	14.33	28.80
Starch (by acid method) .....	16.65	32.04
"Protein" (N x 6.25) .....	2.63	5.44
Total ash (mineral residue) .....	2.35	6.20
Ash insoluble in acid ("sand") .....	0.02	2.42

Several complete analyses of cassia buds have also been made. Results representing three samples examined in America are shown in Table 62. (See next page.)

Table 62. Analyses of Cassia Buds.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	4.79	8.74
Volatile ether extract .....	3.11	4.65
Non-volatile ether extract .....	5.21	6.27
Crude fiber .....	8.60	13.89
Starch (by acid method) .....	10.44	10.98
"Protein" (N x 6.25) .....	7.00	8.00
Total ash .....	4.58	5.58
Ash insoluble in acid ("sand") .....	0.19	0.35

Ground cinnamon, ground cassia, according to Federal standards of purity, "is a powder made from cinnamon and contains not more than five (5) percent of total ash and not more than two (2) percent of ash insoluble in acid." \* The acid-insoluble ash, as said before, is considered as sand, and by noting the above analyses it will be seen that one of the maxima for this item is somewhat above 2 percent. This, however, was a very abnormal sample as the average for twenty-six combined cinnamon and cassia analyses gave much less than 1 percent as the amount of sand to be looked for in ground cinnamon or cassia. The standard, therefore, is very liberal, as is also the standard for the total ash. The average of the thirty-eight combined cinnamon and cassia analyses just mentioned, for total ash, is well below 5 percent.

In Austria, Switzerland and Bavaria the legal standard is: not more than 5 percent total ash nor more than 1 percent sand.

The Federal standard analytical limits do not, of course, demonstrate necessary botanical purity. The definition parts of the standards, however, imply botanical purity, and any foreign vegetable matter is usually detected by the skilled microscopist or can be demonstrated by certain of the chemical determinations.

Thus the addition of foreign starchy adulterants would be quickly shown by the microscope, while foreign barks (few of which contain starch), if not plainly proven by the microscope, would be confirmed by the decided increase in crude fiber and decrease in starch. Elm bark is reported as having been occasionally found, also the more general spice adulterants, such as ground nut shells, olive stones, pea hulls, exhausted cloves and ginger and various cereal products. Few of these would be missed by the experienced food microscopist.

\* The U. S. P. or drug law standard allows in true (Ceylon) cinnamon not more than 3 percent of the outer bark or other foreign matter, not more than 6 percent total ash, nor more than 2 percent of ash insoluble in hydrochloric acid, nor less than 0.5 percent of volatile ether extract. For Saigon cinnamon or cassia not less than 2 percent of volatile ether extract is required and not over 6 percent total ash and 2 percent acid insoluble ash allowed.

## CLOVES

Cloves are the dried, undeveloped flowers of the clove tree, an evergreen of moderate height of the myrtle family and cultivated extensively in tropical regions, particularly Zanzibar, Brazil, Ceylon, India and the Malay peninsula.

The green buds during their growth change to a reddish color, at which stage they are collected and allowed to dry, the color changing to a deep brown. Each whole clove consists of a hard, peg-shaped calyx surmounted with four sepals surrounding a globular casing consisting of tightly rolled petals, stamens, pollen grains and other parts of the flower.

The Federal definition and standard reads as follows: "Cloves are the dried flower buds of *Caryophyllus aromaticus*, L.," which "contain not more than five (5) percent of clove stems; not less than fifteen (15) percent of volatile ether extract; not less than twelve (12) percent of quercitannic acid (calculated from the total oxygen absorbed by the aqueous extract); not more than seven (7) percent of total ash; not more than five-tenths (0.5) percent of ash insoluble in hydrochloric acid, and not more than ten (10) percent of crude fiber."

The U. S. Pharmacopœia standard allows not over 5 percent stems or other foreign matter, not less than 10 percent volatile ether extract, not more than 8 percent total ash nor more than 0.5 percent ash insoluble in hydrochloric acid.

The principal constituent of the analytical item known as volatile ether extract (i.e., matter dissolved out by ether and volatilized at the temperature of boiling water or 10° C. above) is clove oil, the ingredient to which the greater part of the condimental value is due. Oil of cloves is composed of from 70 to 80 percent of a phenol-like chemical compound known as eugenol and several terpenes, particularly caryophyllene.

Cloves also contain some fixed oil and resin (constituting the non-volatile ether extract); a notable and quite constant proportion of tannic acid, and considerable fiber (mainly cellulose); but no starch, although the diastase method of estimating starch shows about 3 percent of compounds very closely related to starch. "Mother cloves," a matured clove tree product, used to some extent for adulterating cloves, contains much starch, the granules of which very closely resemble ginger starch.



Table 63 shows the maximum and minimum limits found in eighty-six analyses of botanically pure cloves, compiled by the author.

Table 63. Clove Analyses.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture* .....	2.90	11.80
Volatile ether extract (oil) .....	11.03	20.53
Non-volatile ether extract .....	4.87	12.00
Quercitannic acid .....	11.28	24.18
"Protein" (N x 6.25) .....	4.20	7.06
"Starch" (by diastase method) .....	2.08	3.15
Crude fiber .....	6.18	9.75
Ash (mineral residue) .....	5.03	13.05
Ash insoluble in acid (sand) .....	0.00	0.13

\* The water in fresh cloves should not exceed 12 percent and in stored cloves not exceed 8 percent.

The minimum figure for quercitannic acid and the maximum total ash figure as given in the table are very rarely met. A clove sample with 13 percent of mineral matter (unfortunately the acid-insoluble ash is not given in the several government analyses which report above 10 percent total ash) is doubtlessly abnormally dirty, but there is good evidence for believing that the limit of .7 percent fixed in the Federal standard should be supported by more data than were evidently considered by the Commission. The 11.28 percent of quercitannic is very low (the great majority of samples range between 16 percent and 20 percent), and the limit allowed in the Federal standard, i.e., 12 percent, is probably liberal enough for all purposes.

As is well known, the most common sophistication of ground cloves is the incorporation of more or less exhausted cloves, the product remaining from the process of preparing oil of cloves. When one considers the range between the Federal requirement comprehending this constituent (viz., "not less than 15 percent of volatile ether extract") and the above, and even higher maximum that has been found, it will be seen that, starting with a clove rich in oil, a fairly large proportion of exhausted cloves can be added without detection, unless, as might sometimes be the case, the crude fiber limit is thereby exceeded.

Another common form of adulteration in cloves is the admixture of an excess of clove stems. The Federal standard provides for a reasonable unavoidable presence of clove stems, viz., 5 percent. The skilled spice microscopist can tell very closely whether this limit has been overstepped, although it is doubtful if strictly chemical methods would prove it unless the adulterant was present in large amount. The most noticeable difference chemically, which would

upset the chemical values for pure cloves, if a considerable admixture were attempted, is the decidedly greater proportion of fiber found in the stems. Table 64 gives the mean results of two analyses of clove stems.

Table 64. Analyses of Clove Stems.

	Percent
Moisture .....	8.74
Volatile ether extract .....	5.00
Non-volatile ether extract .....	3.83
Quercitannic acid .....	18.79
"Protein" (N x 6.25) .....	5.88
"Starch" (by diastase method) .....	2.17
Crude fiber .....	18.71
Ash (mineral residue) .....	7.99
Ash insoluble in acid ("sand") .....	0.60

Added to a clove poor in clove oil, the rather low volatile ether extract figure above reported would preclude the addition of much clove stems. Other adulterants which have been reported as being occasionally found in ground cloves are allspice, exhausted ginger, cereal products, ground nut shells and olive stones and charcoal. Microscopical analysis would quickly demonstrate such crude attempts at sophistication.

### CORIANDER

As defined and standardized in the Federal food standards "Coriander seed is the dried fruit of *Coriandrum sativum*, L. It contains not more than seven percent (7%) of total ash nor more than one and five-tenths percent (1.5%) of ash insoluble in hydrochloric acid." The U. S. Pharmacopœia (Ninth Revision) required coriander, in addition to the same ash limit, to contain at least 0.5 percent of volatile oil (volatile ether extract) and to be 95 percent sound seed, i.e., not more than 5 percent of other seeds or foreign matter. This last requirement is also specified in the import inspection standard, (S. R. A. Item 71). Wormy seeds are considered as foreign matter.

### CUMIN SEED

This spice is defined as "the dried fruit of *Cuminum cyminum* L." containing "not more than nine and five-tenths (9.5%) of total ash, not more than one and five-tenths percent (1.5%) of ash insoluble in hydrochloric acid, nor more than five percent (5%) of harmless foreign matter." A limit for volatile oil is pending investigation.

## DILL SEED

"Dill seed is the dried fruit of *Anethum graveolens* L. It contains not more than ten percent (10%) of total ash, nor more than three percent (3%) of ash insoluble in hydrochloric acid."

## FENNEL SEED

Fennel seed is legally defined as "the dried fruit of cultivated varieties of *Foeniculum vulgare* Hill," containing "not more than nine percent (9%) of total ash, nor more than two percent (2%) of ash insoluble in hydrochloric acid." Service & Regulatory Announcement Item 71 specifies that it should also show not less than 96 percent sound fennel seed, a requirement copied from the U. S. Pharmacopœia. The volatile oil, like that of anise seed, is used in medicine.

## GINGER

Next in order we come to ginger, which, as a spice, is the ground dried rhizome of an annual herb of the family *Zingiberaceæ*, native to India and China, but cultivated quite extensively in tropical America and Africa. The root is dug when the plant is about a year old and the stem has withered. Scalded and dried at once with the skin on, it forms the so-called black ginger of commerce; while that with the skin removed is known as white ginger, the latter often being bleached or sprinkled with carbonate of lime. Jamaica ginger is one, if not the best, of the varieties of white ginger.

White or decorticated ginger is less aromatic than whole or black ginger, as the epidermis of the latter contains considerable pungent resin. The most characteristic chemical constituents of ginger are the large amount of starch and the pungent volatile oil and resins to be found therein. The starch granules under the microscope appear as egg shaped, nearly transparent bodies, having a wart-like protuberance near one end of the long diameter. Volatile oil of ginger is very aromatic, ranging from 0.875 to 0.885 in specific gravity, and being but slightly soluble in alcohol.

The following is the Federal definition and standard for ginger: "Ginger is the washed and dried or decorticated and dried rhizome of *Zingiber officinale* Roscoe," and "contains not less than forty-two (42) percent of starch, not more than eight (8) percent of crude fiber, not less than twelve (12) percent of cold water extract,

not more than seven (7) percent of total ash, not more than one (1) percent of lime (CaO), and not more than two (2) percent of ash insoluble in hydrochloric acid, nor less than two (2) percent of ash soluble in water." "Limed, or bleached, ginger is whole ginger coated with carbonate of lime," and "contains not more than ten (10) percent of total ash, not more than four (4) percent of carbonate of calcium, and conforms in other respects to the standard for ginger." "Jamaica ginger is ginger grown in Jamaica. It contains not less than fifteen (15) percent of cold water extract, and conforms in other respects to the standard for ginger."

There have been many partial and complete analyses of ginger made, especially in State food inspection laboratories, but only a very few of the whole root, with special reference to the use or non-use of lime. Hence, in the following results (Table 65), representing 141 samples pronounced pure in State inspection work, it will appear that the maximum total ash figure found is much above the Federal limit of seven percent. The analysis furnishing this figure also showed a high proportion of carbonate of lime, however, and probably most, if not all, of the analyses showing a total ash decidedly above 6 percent were of ground ginger which had originally been well limed.

Table 65. Analyses of Ginger.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	8.71	12.00
Volatile ether extract (oil) .....	0.96	4.05
Non-volatile ether extract (resins) .....	2.29	8.42
Alcohol extract .....	3.63	9.58
Cold water extract .....	10.92 *	17.55
Starch (diastase method) .....	42.89	60.31
Crude fiber .....	1.70	7.85
"Protein" (N x 6.25) .....	4.81	10.85
Total ash (mineral residue) .....	3.10	9.35
Ash insoluble in acid .....	0.02	2.29
Ash soluble in water .....	2.00	4.02
Lime (CaO) .....	0.20	3.53

\* Kebler and Kimberly (Bureau of Chemistry Bulletin 152) report on 18 varieties of ginger, six of which showed less than 12 percent of cold water extract and four of which showed less than 42 percent starch, several as low as 32 percent starch. Also see *J. A. O. A. C.* for Nov., 1915, for other data on different varieties.

Excepting the minimum figure for cold water extract, it will be noticed that in comparison with the above data the analytical limits fixed in the Federal standards are liberal enough. In our compilation we have included two new analytical items, viz.: the alcohol extract, or substances dissolved out by strong (95%) alcohol, and the cold water extract, or substances dissolved out by cold water.

Both items are of considerable interest and value; first, because they show the amounts of solid matter to be looked for in an official ginger extract (made according to the U. S. Pharmacopœia), and in "ginger ale" respectively; and, second, because they afford evidence as to adulteration with the exhausted ginger remaining after the preparation of the ginger extract or ale. Another item of value for detecting the presence of exhausted ginger from ginger ale manufacture, is the proportion of ash soluble in water, which is usually less than 0.5 percent in the ginger ale residue, but from 1.8 to 4 percent in pure ginger. Allen and Moore\* are quite dogmatic on these points and claim that the presence of exhausted ginger (the ginger ale residue is meant here) is assured when the cold water extract is less than 8 percent and the water soluble ash less than 1 percent. The use of exhausted ginger from ginger extract manufacture would be indicated by the low ether and alcohol extracts. Table 66 shows the analytical nature of both kinds of exhausted ginger.

Table 66. Analyses of Exhausted Ginger.

	Percent	
	<i>Ginger Extract Residue</i>	<i>Ginger Ale Residue</i>
Moisture .....	8.02	10.61
Volatile ether extract .....	0.13	1.61
Non-volatile ether extract .....	0.54	3.86
Alcohol extract .....	1.52	4.88
Cold water extract .....	16.42	6.15
Starch (diastase method) .....	....	54.57
Crude fiber .....	....	5.17
"Protein" (N x 6.25) .....	....	6.94
Total ash .....	5.05	1.1 to 2.12
Ash soluble in water .....	3.55	0.2 to 0.59
Ash insoluble in acid .....	1.50	0.18

Other adulterants of ginger that have been found in food inspection work are turmeric, cereal products and sawdust. The presence of turmeric would be demonstrated either with the microscope or by the well-known boric acid test, and the characteristic shape of the ginger starch granules would enable the easy microscopic recognition of all other starch-containing substances (cereals, etc.), save mother cloves, the use of which would be impracticable unless exhausted and bleached. Sawdust, if used to any extent, would greatly increase the crude fiber value, and would also be shown by a careful microscopical study of the fiber cells.

The U. S. Pharmacopœia requires not less than 8 percent of cold

\* *Analyst*, 19, 194 (1894).

water extract, not less than 2 percent non-volatile ether extract, not less than 4 percent alcohol-soluble extract and not more than 1 percent total ash.

### HORSERADISH

Horseradish is legally defined in the Federal standards as "the root of *Radicula armoracia* (L), Robinson, either by itself or ground and mixed with a vinegar." At present no analytical limits are called for, not even the kind of vinegar to be used being stated, although considerable confusion and some forms of adulteration exist in the trade. One of the principal forms of the latter is the use in the ground bottled product of more or less cornstarch paste, usually in a quite small proportion, to give the vinegar a milky color, but sometimes in considerable amount as a "filler," or absorber of excess of vinegar.

Owing to the fact that the dry solid matter of the horseradish root is, to a large extent, composed of starch (quite small, football shaped, microscopical granules), it would be difficult, if not impossible, to estimate the added starch chemically, but with the microscope a fairly close approximation of the foreign starch might be made, provided the latter had not been cooked to the extent of destroying its histological structure.

The pungent volatile oil so characteristic of a freshly cut horseradish root somewhat resembles in composition that of mustard seed, containing evidently, like the latter, a certain proportion of sulfur, which gives by the official method a test resembling that given by sulfurous acid, a fact which has misled several careless State chemists into making the rather absurd accusation that a preservative had been used in the horseradish examined by them. The most likely form of adulteration to be looked for in bottled or ground horseradish is the substitution of other roots, especially turnip or white beets, and the addition of synthetic "mustard oil."

### MACE

Mace is frequently but not necessarily considered in connection with nutmeg, it being the drilled arillus surrounding the seed (nutmeg) of a certain variety of the genus *Myristica*, a tree from twenty to thirty feet high, native to the Malay archipelago. The Federal standard plainly indicates that neither Macassar, Papua nor Bombay mace (also called wild or false mace) can be regarded as the spice

under discussion, by specifically defining mace as "the dried arillus of *Myristica fragrans*, Houttuyn," which should contain "not less than twenty (20) nor more than thirty (30) percent of non-volatile ether extract, not more than three (3) percent of total ash, and not more than five-tenths (0.5) percent of ash insoluble in hydrochloric acid, and not more than ten (10) percent of crude fiber."

Macassar mace, or Papua mace, is defined as "the dried arillus of *Myristica argentea*, Warb," while the almost inert Bombay mace,\* so frequently used to adulterate true mace, was originally defined as "the dried arillus of *Myristica malabarica*, Lamarek."

Mace contains no starch, but does contain a notable quantity of a dextrin very closely related to starch and appearing under the microscope as minute spherical granules, which are colored a reddish brown by iodine solution. Like starch, this dextrin, sometimes called amylopectin, can be estimated by the diastase method. Mace also contains a generous proportion of fixed oil or fat and some resin, constituting together the analytical item known as non-volatile ether extract. In Macassar and Bombay maces this item is more than doubled, hence a quite small addition of Bombay mace to true mace is chemically apparent. Moreover, under a high-power microscope, a true mace shows a pale yellow or grayish mass of loose texture, while Bombay mace shows many dark red and bright yellow lumps of resin. The so-called Hefelmann test for Bombay mace is worthless, as the same reaction is given by many, if not all, true maces.

The volatile oil of mace is very fragrant and is completely, though very slowly, driven off by heat, even after being extracted with ether. It closely resembles nutmeg oil, chemically.

Table 67 shows the maximum and minimum results of ten analyses of pure mace examined or compiled by the author.

Table 67. Analyses of Mace.

	Percent	
	Minimum	Maximum
Moisture .....	4.86	14.60
Volatile ether extract .....	4.04	11.07
Non-volatile ether extract .....	21.63	29.61
Dextrin (diastase method) .....	23.12	30.43
Crude fiber .....	2.94	8.93
"Protein" (N x 6.25) .....	4.55	7.00
Total ash (mineral residue) .....	1.81	4.10
Ash insoluble in acid .....	0.00	0.61

Similar to all of the Federal spice standards, we have considered thus far, the limits fixed are liberal enough (too liberal in some cases)

\* Service and Regulatory Announcement, Item 352 prohibits the sale of Bombay mace as a spice.

except in the total ash figures, wherein the commission have somewhat arbitrarily decided upon limits not borne out by reported analyses of pure, high quality products. For example, the above maximum figure for total ash was obtained by Dr. Wiley's predecessor on a sample of clean *whole* mace. The author has also examined several whole maces, which gave total ash values decidedly above the 3 percent limit called for in the Federal standards.

The commonest adulteration of mace, as intimated above, is the addition of Bombay mace. The analyses of Macassar and Bombay mace shown in Table 68 are of interest.

Table 68. Analyses of Macassar and Bombay Mace.

	Percent	
	<i>Macassar Mace</i>	<i>Bombay Mace</i>
Moisture .....	4.18	0.32
Volatile ether extract .....	5.89	4.65
Non volatile ether extract .....	53.54	59.81
Dextrin (diastase method) .....	8.78	14.51
Crude fiber .....	4.57	3.21
"Protein" (N x 6.25) .....	7.00	5.06
Total ash (mineral residue) .....	2.01	1.98
Ash insoluble in acid .....	0.03	0.07

Another common adulteration of mace is the addition of ground nutmeg, sometimes in large proportion. The microscope quickly shows this form of sophistication, however, as nutmeg contains considerable (15 to 25%) true starch, which has a very characteristic appearance under a strong magnification. Of course, traces of nutmeg starch should be disregarded by the spice microscopist as the same are due to an unavoidable introduction of small fragments of nutmeg occasionally adhering to the mace arillus. Other adulterations reported are turmeric, cereal products and, in whole mace, fragments of a bright red seaweed, closely resembling the mace arillus.

The National Formulary requires mace to be free from Bombay mace, to contain not less than 8 percent volatile ether extract, not less than 20 percent nor more than 30 percent non-volatile ether extract, nor more than 3 percent of total ash.

### MARJORAM

The Federal standards define Marjoram as "the dried leaf and flower-tops of *Majorana hortensis* Moench." Food Inspection Decision 194 calls for "not more than sixteen (16) percent of total ash, not more than four and five-tenths (4.5) percent of ash insoluble in



hydrochloric acid, nor more than ten (10) percent of stems and harmless foreign material."

#### MUSTARD SEED (Also see Chapter IV)

Three different varieties of mustard seed are defined in the Federal standards, viz.: "The seed of *Sinapis alba* (L.) (white mustard); *Brassica nigra* (L.) Koch (black mustard), and *Brassica juncea* Hook f. et Th., or varieties or closely related species of *Brassica nigra* and *juncea*." In their chemical composition there is a distinct difference between ordinary white (or yellow) mustard seed and black or brown mustard seed. The white (or yellow) seeds contain somewhat less fatty oil and a more uniformly low percentage of fiber than do the brown seeds. The principal difference, however, is in the nature of the chemical constituents which yield the powerful volatile oil when the whole seed (more particularly the black or brown seed) is ground and mixed with water.

Both white and black seeds contain an alkaloid known as sinapin sulfo cyanide, a ferment or enzyme known as myrosin, and no starch. Black mustard seeds, however, contain a glucoside, known as sinigrin, not found in white mustard seeds; while the latter contain a glucoside known as sinalbin. When the seeds (especially the black seeds) are ground and moistened the ferment myrosin is enabled to come in contact with and react with the glucoside (sinigrin) to form about 1.2 percent of the well-known volatile oil of mustard, known chemically as allyl sulfo cyanide or isothiocyanate. It has a powerful odor and is capable of blistering the skin. The glucoside in white mustard (sinalbin) reacts with the ferment myrosin, when the seeds are ground with water to form traces of a somewhat similar but distinctly different volatile oil.

The fixed or fatty oil of mustard is a bland, tasteless, pale yellow oil, which has been used as a table oil, but is more generally used for illuminating purposes. It is found in the whole seed ranging from about 22.5 percent in white mustard to as high as 39 percent in certain brown mustards and 43 percent in Oriental yellow seed. In the manufacture of ground mustard, or mustard "flour," a large proportion of this fatty oil is removed by pressure, as is evidenced below by the analytical data on ground commercial mustard, or mustard flour.

It is also customary to remove a certain proportion of the mustard hulls in the manufacture of mustard "flour." These removed hulls or

bran are frequently incorporated, however, into prepared mustard, constituting an adulteration of the latter which the Federal standard, as we have seen, will not usually accommodate. In connection with prepared mustard (see Chapter IV), we have gone rather extensively into the legal chemistry of the various mustard products, which the Federal standards list, viz.: *Sinapis alba* (white or yellow mustard), *Brassica nigra* (black and brown mustard), *Brassica juncea* (and varieties and closely related species), Ground Mustard Seed or Mustard Meal, Mustard Cake, and Mustard Flour or Ground Mustard; and we will not try to repeat all the data here.

It will be of interest, however, to see how different varieties of mustard seeds analyze, especially the newer Oriental seeds, both on the basis of the original seed and on the dry, fat-free basis. The data in Table 69, determined by R. Hertwig and T. O. Kellems of the San Francisco laboratory of the U. S. Bureau of Chemistry, represent 18 samples of English, California, Dutch and Danish yellow mustard seeds; 15 samples of English, California, Italian and South American brown mustard seeds and 10 samples of Chinese and Japanese yellow seeds (*Brassica cernua*), the latter being similar to the brown seeds in yielding a notable percentage of a volatile oil of mustard,\* whereas ordinary yellow seeds yield only a trace.

We have spoken of the significance of the data on nitrogen, phosphoric acid, calcium oxide and magnesium oxide and the various ratios in connection with prepared mustard (see Chapter IV) and it is by these data that it will be possible to establish the presence of an excess of mustard hulls (bran) more surely than by the percent of crude fiber (or ratio of same to dry and fat-free solids) alone.

It will be noticed that the Oriental yellow seeds (*Brassica cernua*) show distinctly less crude fiber than either the ordinary yellow seeds (*Sinapis alba*) or the various black and brown seeds. The maximum (on the dry, fat-free basis) for Oriental yellow seeds is 8.3 percent (which is practically the minimum for the other seeds) and in a prepared mustard made from Oriental seed largely, such as is the case in several well-known brands, it is peculiar that the crude fiber (figured to dry, salt-free and fat-free basis) is always up around 11 to 12 percent, just within the Federal prepared mustard standard limit for crude fiber. Such cases are illustrations of the need of other data and ratios, such as referred to above, for proving that excess bran is present even though the standard limit for crude fiber has been complied with.

\* Said to be crotonyl sulfocyanide.

Table 69. Analyses of Mustard Seeds.

	Percent					
	<i>Sinapis alba</i> (Yellow)		<i>Brassica nigra</i> (Brown)		<i>Brassica oleracea</i> (Oriental)	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Original Seeds						
Moisture .....	8.71	6.23	8.19	6.63	7.34	5.63
Fatty Oil .....	32.36	26.01	39.85	29.48	43.76	33.70
Nitrogen .....	5.43	3.93	4.83	3.51	4.39	3.90
Crude Fiber .....	6.64	5.28	6.87	4.81	4.48	3.94
Volatile Mustard Oil ....	0.06	0.04	1.32	0.55	0.88	0.65
Total Ash .....	5.47	3.57	8.97	3.68	8.41	3.89
Water-insoluble Ash ....	4.66	2.73	8.46	3.07	7.99	1.85
Acid-insoluble Ash .....	0.48	0.00	3.66	0.06	4.86	0.11
Total Phosphoric Acid....	2.57	1.50	2.47	1.66	1.96	1.28
Calcium Oxide .....	0.786	0.478	1.014	0.516	0.583	0.448
Magnesium Oxide .....	0.626	0.401	0.717	0.529	0.640	0.449
Moisture- and Fat-Free Basis						
Nitrogen .....	8.35	6.52	8.00	6.42	7.90	7.21
Crude Fiber .....	11.0	8.1	11.0	8.0	8.3	7.2
Total Phosphoric Acid....	4.13	2.30	4.40	2.92	3.91	2.28
Calcium Oxide .....	1.298	0.734	1.734	0.855	1.075	0.797
Magnesium Oxide .....	0.984	0.616	1.326	0.849	1.251	0.798
Ratios						
Nitrogen/Crude Fiber....	1.00	0.59	1.00	0.56	1.02	0.87
Phosphoric Acid/Crude Fiber .....	0.46	0.28	0.42	0.28	0.49	0.30
Magnesium Oxide/Crude Fiber .....	0.10	0.07	0.13	0.08	0.16	0.10
Calcium Oxide/Magnesium Oxide .....	1.69	0.96	1.71	0.84	1.06	0.79
Ratio A* .....	0.64	0.29	0.78	0.27	0.46	0.26
Ratio B† .....	0.88	0.32	0.78	0.29	0.44	0.21

\* Ratio A is the Calcium Oxide multiplied by the Crude Fiber and divided by the Phosphoric Acid (as  $P_2O_5$ ) after multiplication of the latter by the Nitrogen.

† Ratio B is Ratio A divided by the Magnesium Oxide.

The data on fatty oil show that the Oriental seeds run higher in this constituent and the data on volatile oil illustrate clearly the decided condimental difference between the ordinary yellow seeds (averaging 0.05 percent volatile oil, as allyl isothiocyanate) and the brown and Oriental yellow seeds showing from twelve to twenty-six times greater yield of volatile (flavoring) oil. Yet other constituents in the ordinary yellow seed (*Sinapis alba*) give it a condimental value that has been long recognized.

In connection with the exhaustive analyses, by Hertwig and Kellems, of different varieties of mustard seeds, there were determined also similar data on 19 samples of commercial mustard brans (hulls as separated in the manufacture of mustard flour) which we give here for completeness of data (Table 70) and to show how the above-mentioned ratios will be affected by the presence of added

bran. For more data the reader should consult the *Journal of the Association of Official Agricultural Chemists* for August and November of 1923.

Table 70. Analyses of Commercial Mustard Brans.

Original Material	Percent	
	Minimum	Maximum
Moisture .....	7.29	10.56
Fatty Oil .....	8.47	18.29
Nitrogen .....	2.53	4.52
Crude Fiber .....	10.77	25.18
Volatile Oil of Mustard .....	....	0.33
Total Ash .....	4.29	5.68
Water-insoluble Ash .....	1.95	3.54
Acid-insoluble Ash .....	0.02	0.61
Total Phosphoric acid ( $P_2O_5$ ) .....	0.572	1.851
Calcium oxide ( $CaO$ ) .....	0.644	1.518
Magnesium oxide ( $MgO$ ) .....	0.263	0.605
Moisture- and Fat-Free Basis		
Nitrogen .....	2.70	5.92
Crude Fiber .....	14.1	29.2
Total Phosphoric acid ( $P_2O_5$ ) .....	0.69	2.42
Calcium oxide ( $CaO$ ) .....	0.862	1.910
Magnesium oxide ( $MgO$ ) .....	0.328	0.792
Ratios		
Nitrogen/Crude Fiber .....	0.09	0.42
$P_2O_5$ /Crude Fiber .....	0.01	0.17
$MgO$ /Crude Fiber .....	0.01	0.06
$CaO/MgO$ .....	1.2	4.9
Ratio A* .....	1.3	23.4
Ratio B* .....	1.6	61.4

\* See references under Table 69.

The Federal standards, as amended by Food Inspection Decision 192, define a "Ground Mustard Seed" or "Mustard Meal" as "the unbolted, ground mustard seed and conforms to the standards for mustard seed." "Mustard Cake is ground mustard seed or mustard meal from which a portion of the fixed (fatty) oil has been removed."

Ground mustard as sold commercially is defined and standardized as follows: "Mustard Flour, Ground Mustard, "Mustard," is the powder made from mustard seed with the hulls largely removed and with or without the removal of a portion of the fixed (fatty) oil. It contains not more than one and five-tenths percent (1.5%) of starch, nor more than six per cent (6%) of total ash."

The limit for total ash should be at least one percent higher and, if the data determined on brown and Oriental mustard seeds (by Hertwig and Kellems of the U. S. Bureau of Chemistry) are taken into consideration, the 5 percent limit for total ash in the Federal standards for *Brassica nigra*, *Brassica juncea* and varieties and closely

related species of the same, should be raised to 9 percent. The U. S. Pharmacopœia (Ninth Revision) allows 9 percent ash in both *Sinapis alba* (white or yellow mustard) and *Brassica nigra* (black mustard). Hertwig and Kellems also reported brown and Oriental mustard seeds with two and three times as much acid-insoluble ash as is allowed in the mustard seed standards, i.e., 1.5 percent.

The U. S. Pharmacopœia allows not over 5 percent of foreign seeds to be present and the U. S. import inspection allows the same limit. Certain weed seeds are quite rich in starch; moreover mustard seed, although it contains no true starch, does show a small proportion of substances which upon analysis appear as "starch" by the legal diastase method of estimating starch. It would seem therefore, and our analyses (see below) of pure mustard flours support it, that the 1.5 percent starch limit of the Federal standard for "Mustard Flour" or "Ground Mustard" should be raised one percent also. This limit is simply for the purpose of accommodating the accidental traces of weed seed starch and of course the microscope will quickly demonstrate any material adulteration with starchy matter.

Table 71 represents 23 samples of pure commercial ground mustards (or mustard flours) examined in the Massachusetts and Connecticut food inspection departments.

Table 71. Analyses of Ground Mustards (Mustard Flours).

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	5.09	9.50
Non-volatile ether extract (fatty oil) .....	12.65	38.47
Alcohol extract .....	19.22	25.31
"Protein" (N x 6.25) .....	35.63	46.50
Crude fiber .....	1.58	4.87
Starch (diastase method) .....	0.00	2.08
Total ash (mineral residue) .....	4.36	7.35
Ash insoluble in acid .....	0.08	0.50

The most common adulteration in earlier days was the addition of cereal flours, especially wheat flour; excess of finely ground hulls and turmeric. The last was used in small proportion for coloring purposes—either to restore color when a cereal adulterant had been added, or to give to naturally pale-yellow pure mustard the vivid yellow color usually wanted by the buying public.

Other adulterations of both whole mustard seeds and of meals and flours made from them, are the accidental and intentional additions (sometimes complete substitution), of certain rapeseeds and wild

mustard seed or charlock. The latter analyzes almost identical with *Sinapis alba* (ordinary yellow or white mustard). In Chapter IV under "Prepared Mustard" are given the comparative analyses of various rapes and charlock (*Sinapis arvensis*) and details and remarks upon the use of the same, especially in prepared mustard.

### PREPARED MUSTARD

This condimental sauce is standardized under the spices in the Federal standards. We have dealt with it quite fully in Chapter IV, which see.

### NUTMEG

Nutmeg being a product of the same tree as mace—both, in fact, being very closely associated, as the seed of the nutmeg fruit and its covering, or arillus—they are frequently taken up together in a food chemistry manual. In the Federal standards of purity for food products (Circ. 136, Office of Secretary, U. S. Dept. of Agriculture), however, the alphabetical arrangement is adhered to, and thus, following the various mustard standards, we now come to nutmeg specifically defined as "the dried seed of *Myristica fragrans*, Houttuyn, deprived of its testa, with or without a thin coating of lime."

If up to legal requirements, it must contain "not less than twenty-five (25) percent of non-volatile ether extract, not more than five (5) percent of the total ash, not more than five-tenths (0.5) percent of ash insoluble in hydrochloric acid, and not more than ten (10) percent of crude fiber.\* Macassar nutmeg, Papua nutmeg, male nutmeg or long nutmeg (these, and not the word "nutmeg" alone, being the names required when offered for sale) is defined as "the dried seed of *Myristica argentea*, Warb, deprived of its testa." Not more than 20 percent of any whole nutmegs may show mold.

Nutmeg contains considerable starch, which from a micro-chemical standpoint immediately distinguishes it from mace, which contains none. The starch granules under a high-power microscope appear as circular grains, quite uniform in size (about 5 to 6 microns in diameter), and show a distinct central dot or hilum.

The most plentiful constituent of nutmeg, however, is the fatty oil present to the extent of from 25 to 40 percent. Associated with it in the analytical item known as total ether extract is a volatile oil with characteristic odor and flavor, soluble in about three times

\* The U. S. P. or drug law standard calls for not over 5 percent total ash and all broken or wormy nutmegs to be rejected.

its weight of strong alcohol. The specific gravity of volatile nutmeg oil ranges from 0.860 to 0.920.

Under the microscope a ground nutmeg sample shows numerous red and deep yellow bits of resinous matter, similar to those appearing in ground Bombay mace. Therefore, the spice microscopist should assure himself of the absence of nutmeg starch granules before declaring a true mace sample to be adulterated with Bombay mace, even though the fatty oil content be also suggestive of Bombay mace. Nutmeg, as said in connection with the mace standard, is frequently used to adulterate ground mace, and a trace of nutmeg in mace is almost unavoidable.

Whether Bombay mace is used to adulterate ground nutmeg, the author can not say, although the above microscopical similarity, and particularly the similarity in chemical analytical data, would make such a practice (to a moderate extent) not easy of certain detection, especially as nutmeg gives (similar to all maces) the so-called "Hefelmann test for Bombay mace." A careful microscopical search for the "amylodextrin" granules, characteristic of the maces and not colored blue with iodine solution, as are the nutmeg starch granules, together with a comparative study of the analytical item known as alcohol extract, would perhaps demonstrate such an adulteration. An analysis of Bombay mace made by Winton showed 44.27 percent alcohol extract (Macassar mace 32.89 percent), while four pure nutmeg samples ranged from 10.42 to 17.38 percent alcohol extract. The difference in non-volatile ether extract between Bombay or Macassar mace and nutmeg, while considerable, would not show a moderate adulteration with certainty.

The analytical data in Table 72 show the minimum and maximum limits found in four samples of pure nutmeg analyzed by the author and eight compiled analyses.

Table 72. Nutmeg Analyses.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	4.19	12.20
Volatile ether extract .....	1.73	10.58
Non-volatile ether extract (fat) .....	26.62	37.30
Alcohol extract .....	10.42	17.38
"Protein" (N x 6.25) .....	5.16	7.00
Starch (diastase method) .....	14.62	24.20
Crude fiber .....	2.38	5.81
Total ash (mineral residue) .....	2.13	4.10
Ash insoluble in acid .....	0.00	0.08

It will be seen that the Federal standard for nutmeg throughout is very liberal. Only an excessive use of lime would bring the total ash figure above the legal limit.

Ground nutmeg is variously adulterated, Macassar nutmeg, cocoanut shells, cereal products, and even woody fiber, having been reported in State food inspection analysis. The microscope will frequently completely demonstrate such impurities.

### BLACK PEPPER

As defined and standardized in the Federal standards: "Black pepper is the dried immature berry of *Piper nigrum*, L." and "contains not less than six and seventy-five hundredths (6.75) percent of non-volatile ether extract, not less than thirty (30) percent of starch, not more than seven (7) percent of total ash and not more than one and five-tenths (1.5) percent of ash insoluble in hydrochloric acid." Ground black pepper is "the product made by grinding the entire berry, and contains the several parts of the berry in their normal proportions." \*

The pepper plant is a perennial climbing vine, native to Southern India, but long and extensively cultivated in Ceylon and the Malay Peninsula and adjacent islands, particularly Sumatra and Java. The fruit is a small, round berry, growing in a cluster of from twenty to thirty in number. To obtain black pepper the berries are picked when first beginning to turn red, and are dried in the sun or near a fire, which process causes them to turn black and the outer fleshy coating to shrivel and harden to a wrinkled cortex or "shell."

Sometimes the berries are spread upon the bare ground to dry, and from unavoidable adhering dirt, or dirt which is carelessly scooped up with the dried berries, may yield an excessive proportion of ash or mineral matter upon subsequent analysis. Just where to draw the line between an allowable and excessive proportion of mineral matter in pepper is a much argued subject. The ash insoluble in hydrochloric acid (sometimes reported as "sand") is abnormally high in such dirty peppers, particularly in certain grades of Acheen, or pepper from the western extremity of Sumatra.

Pepper contains considerable starch, as our analyses will show. Under the microscope the starch granules (minute polygonal particles,

\* The U. S. P. or drug law standard specifies not over 2 percent stems or other foreign matter, not less than 6 percent of non-volatile ether extract, not less than 25 percent starch, not over 7 percent total ash and not more than 2 percent of ash insoluble in hydrochloric acid.



averaging 3 microns in diameter) are usually found grouped in large coffin-shaped masses. A rather fragrant volatile oil, of terpene constitution, and an ether and alcohol soluble alkaloid, known as piperin,  $C_{17}H_{19}NO_3$ , present to the extent of about 4 to 7 percent, have much to do with the flavor and pungency of pepper. In analysis the piperin constitutes the greater part of the non-volatile ether extract and accounts for the high nitrogen content of the same. The former standard fixed a minimum limit for this nitrogen, viz., 3.25 parts in 100 parts of non-volatile ether extract.

Varieties of black pepper are named from the different localities in which they grow or are shipped, as Singapore, Acheen, Tellichery, Lampong (east end of Sumatra), or sometimes are given a special trade name after being prepared by a special process—for example, Shot pepper and Mangalore pepper.

Black pepper in general (excepting possibly Acheen) has the same analytical characteristics, irrespective of its source. However, as considerable data on the different varieties and grades are at hand, we will, in our compilation of analyses, go into detail somewhat. A few notes on certain varieties are appropriate first. A variety which constitutes a considerable proportion of all the pepper raised is Singapore pepper. It is generally dried over smoke—frequently the smoke from the boiling down of gambier, which gives the pepper a characteristic smoky smell, often retained by the ground pepper.

Tellichery, Malabar and Allepey peppers come from India and are sun-dried, being of a light-brown color. Lampong pepper (from the eastern extremity of Sumatra) is also sun-dried, ununiform in size, of light color and frequently dirty. Trang pepper, from Penang, is grown in Japan and Sumatra. Shot pepper are the heavy berries (usually of Singapore) separated by a column or blast of air and oiled to improve appearance. Mangalore are usually large berries, of deep black color, very clean and uniform in size, and yielding a greenish-black ground pepper.

The Acheen peppers were formerly known as "West Coast" and as Sumatra pepper. They are now designated, according to gravity, as grade or class A, B, C and D, the first weighing 481 grams to the liter and the last 356 grams to the liter. They are distinctly of lighter weight, containing more or less empty berries, and often an excess of dirt, especially the C and D grades.

The analyses of pure whole peppers shown in Table 73 are principally those made by the Connecticut and Michigan food inspection departments in 1898 and 1902. A brief examination of the table

Table 73. Analyses of Black Peppers.

Variety, etc.	Moisture	Percent							Weight in Grams per 100 Berries
		Volatile Ether Extract	Non-volatile Ether Extract	Starch (Diastase Method)	Crude Fiber	Parts Nitrogen in 100 Parts Non-volatile Extract	Total Ash (Mineral Residue)	Ash Insoluble in Hydrochloric Acid	
<i>Singapore</i> (14 Samples)—									
Minimum .....	8.20	0.99	6.57	33.75	10.02	3.91	3.09	0.07	3.90
Maximum .....	12.43	1.94	7.92	39.66	13.82	4.22	4.95	0.56	5.46
<i>Tellicherry</i> (7 Samples)—									
Minimum .....	8.42	0.65	6.72	36.03	11.98	3.88	4.06	0.00	4.13
Maximum .....	11.86	1.55	7.90	41.75	13.21	4.14	4.69	0.10	5.11
<i>Allepey</i> (5 Samples)—									
Minimum .....	8.46	1.12	7.48	34.65	11.36	3.72	4.74	0.07	4.29
Maximum .....	10.01	1.90	8.87	41.60	13.01	3.98	5.02	0.30	5.41
<i>Malabar</i> (2 Samples)—									
Minimum .....	9.47	1.04	6.10	36.84	9.68	3.86	3.45	0.09	4.23
Maximum .....	10.53	1.51	7.71	44.83	12.78	4.00	4.40	0.20	5.74
<i>Lampung</i> (10 Samples)—									
Minimum .....	8.09	1.11	6.81	33.41	10.25	3.82	4.86	0.48	3.32
Maximum .....	12.17	2.10	9.05	39.46	13.50	4.27	6.52	1.80	3.79
<i>Trang</i> (5 Samples)—									
Minimum .....	8.09	1.22	6.60	35.73	10.58	3.79	3.43	0.33	3.82
Maximum .....	11.57	1.60	8.27	41.00	13.11	4.10	4.16	0.41	4.13
<i>Acheen A</i> (3 Samples)—									
Minimum .....	8.73	1.09	9.17	28.00	13.07	4.02	5.04	0.48	3.20
Maximum .....	12.09	1.71	10.44	33.72	16.97	4.21	6.49	0.96	3.69
<i>Acheen B</i> (3 Samples)—									
Minimum .....	8.89	1.15	9.03	25.09	14.09	4.06	5.80	1.15	2.52
Maximum .....	12.95	2.07	9.72	33.08	18.84	4.13	6.62	1.36	2.79
<i>Acheen C</i> (4 Samples)—									
Minimum .....	9.62	1.28	8.99	22.05	16.40	3.94	6.10	1.00	2.12
Maximum .....	12.33	2.05	10.20	33.38	18.25	4.18	8.04	2.59	2.82
<i>Acheen D</i> (2 Samples)—									
Minimum .....	10.03	1.66	8.24	28.00	17.98	4.05	6.75	1.52	.....
Maximum .....	10.06	1.98	8.81	28.40	18.89	4.15	7.00	1.62	2.46
<i>Mangalore</i> (3 Samples)—									
Minimum .....	8.53	1.50	6.81	34.62	10.00	3.46	4.03	0.05	8.57
Maximum .....	11.61	1.87	9.08	36.95	10.42	4.06	4.74	0.19	9.72
<i>Shot Pepper</i> (3 Samples)—									
Minimum .....	8.40	1.16	6.66	33.19	10.58	3.29	3.66	0.20	4.84
Maximum .....	11.50	1.44	7.49	38.60	13.04	4.07	4.15	0.28	6.00

will plainly show that, except for the various Acheen peppers, the Federal standard limits are liberal, even with respect to the much discussed total ash limit. The Acheen peppers, however, particularly the B, C and D grades, constitute a special class by themselves. The high ash and acid insoluble figures have been explained by the method of drying. The very high crude fiber values are doubtless due to the many empty berries found in Acheen peppers, while the starch content would decrease proportionately for the same reason. Probably the rather high non-volatile ether extracts are explained in the same manner.\*

The fact remains, however, that, excepting the non-volatile ether extract limit, it is entirely possible and likely that a sample of Acheen pepper, considered pure from the spice trade standpoint, might transgress the Federal standard for black pepper throughout. That this fact should be recognized in the Federal spice standards seems obvious.

Probably no spice has been subjected to the variety and extent of adulteration as ground black pepper. The list of adulterants is unique and endless. Ground nut shells of all kinds (especially cocoa-nut shells), ground olive stones, date stones, charcoal, crackers, cayenne, buckwheat middlings and cereal products of all kinds, sand, factory sweepings and even coal are some that may be mentioned. In earlier days the author found many samples composed of adulterants to the extent of 80 or 90 percent. The microscope usually reveals such crude adulterants.

The most prevalent form of sophistication is the addition of pepper shells, the by-product obtained from the manufacture of white pepper, which is the mature pepper berry with the shell removed. It is possible to mix in quite a large proportion of shells without risk of definite detection, under certain conditions, but usually the practice is demonstrated by the resulting abnormal crude fiber or low starch figure.

The analytical data on pepper shells shown in Table 74 may prove of interest. (See next page.)

#### POPPY SEED

Poppy seed is officially defined (in Item 195 of Service and Regulatory Announcement No. 19) as "the seed of *Papaver somniferum*

\* The author separated out and tested some completely empty Acheen pepper berries. Non-volatile ether extract was 10.95 percent, volatile ether extract was 2.65 percent and crude fiber was 25.75 percent. This would indicate that the despised light weight berries were the most valuable from the flavoring standpoint, due to loss of conditionally worthless starch. Data reported by Frear showed non-volatile ether extract and piperin to be most plentiful in the second and third (inner) layers of shell.

Table 74. Pepper Shells (seven samples).

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	7.00	11.01
Volatile ether extract .....	0.68	1.11
Non-volatile ether extract .....	1.51	4.97
Starch (diastase method) .....	2.30	*15.30
Crude fiber .....	21.06	32.15
Total ash .....	7.82	*28.81
Ash insoluble in acid .....	0.79	*22.90
Nitrogen in 100 parts of non-volatile ether extract .....	1.90	3.01

\* Exceptional.

L. containing not more than 3 percent of harmless foreign material, not more than 8 percent total ash and not more than 1.5 percent of ash insoluble in hydrochloric acid." It has been found in commerce artificially colored to pass as a more expensive variety. S. R. A. Item 179 forbids more than 0.05 percent of henbane seed.

#### SAFFRON

Saffron is used mainly as a yellow vegetable color, but is classed as a spice. It is defined in the Federal standards (Circular 136) as the "dried stigma of *Crocus sativus* L." containing "not more than ten percent (10%) of yellow styles and other foreign matter, not more than fourteen percent (14%) of volatile matter when dried at 100° C., not more than six percent (6%) of total ash, nor more than one percent (1%) of ash insoluble in hydrochloric acid." The National Formulary, or drug law standard, is the same except that 7.5 percent of total ash is tolerated. Very recently the Federal standard limit for total ash has been raised to 7.5%.

Saffron is a very expensive product and it is subject to extensive adulteration. Formerly mineral make-weights were extensively added (which were easily detected by an ash test), then glycerin was used and more recently honey and sugar have been used, which, inasmuch as the stigmas of a flower contain frequently considerable sugar, constitute a shrewd adulteration.

In recent years considerable analytical work has been done on saffron and the data in Table 75 are characteristic of the pure product. (See next page.)

Fromme\* has devised some tests on saffron, including a fermentation test for fermentable sugars, and claims that there should be not over 6 percent fermentable sugars in pure saffron. Possibly in the following data there are included in the item "reducing sugar"

\* *Apoth. Z.*, 29, 737-9 (1914).

Table 75. Saffron Analyses.

	Percent		
	Minimum	Maximum	Average
Moisture (loss at 100° C.) .....	6.3	16.4	12.5
Total ash (on dry basis) .....	4.5	8.6	6.4
Water soluble (on dry basis) .....	51.4	66.7	60.0
Reducing sugar (on dry basis) .....	8.5	18.8	14.1
Sucrose (on dry basis) .....	0.0	3.7	1.6
Ether extract (on dry basis) .....	0.9	1.5	1.2
Nitrogen (original material) .....	2.2	2.5	2.3

other substances which reduce an alkaline copper salt solution, but if any appreciable proportion of honey, glucose or sucrose has been added as a make-weight there will be found (on the dry basis) more than 19 percent of "reducing sugar," or more than 3.7 percent of sucrose (calculated from the increase in "reducing sugar" after inversion with acid). In fact, the above average values are a liberal enough guide.

The substitution of parts of other flowers was formerly (and is yet) a frequent form of sophistication. Service and Regulatory Announcement, No. 26, Item 339, calls attention to the use of the flower tops (corolla, stigmas and anthers) of cotton or Scotch thistle (*Onopordon* species), artificially colored with coal tar dyes, and safflowers and dyed marigold flowers are also used. The stigmas of *Crocus vernus*, L. (ordinary spring variety) have little odor or taste and but little tinctorial power and, as the work of picking would be just as great, are not substituted much if any. Other vegetable adulterants mentioned are flowers of *Arnica montana*, *Scolymus hispanicus*, and *Punica granatum* and, in powdered saffron, turmeric and annatto. These are all detected by microscopical examination, or by soaking the dried material, when added color is lost and natural form restored.

#### SAGE

This spice is legally defined as "the dried leaf of *Salvia officinalis* L." containing "not less than one percent (1%) of volatile ether extract, not more than twenty-five percent (25%) crude fiber, not more than ten percent (10%) of total ash, nor more than one percent (1%) of ash insoluble in hydrochloric acid." Another official requirement is that the stems (excluding petioles) and other harmless foreign matter are not to exceed 12 percent (S. R. A. No. 19).

American sage averages about 1 percent of essential oil (volatile ether extract) while the Dalmatian sage averages nearly 10 percent. A Service and Regulatory Announcement (No. 23, Item 277)

deals with the substitution of so-called Greek and Spanish sage for *Salvia officinalis* L. Greek sage is *Salvia triloba* L., while Spanish sage is *Salvia lavandulæfolia* Vahl, and it is held that "sage," without any qualifications, applies only to material (leaves) obtained from *Salvia officinalis* L. Greek and Spanish sage are required to be sold as such.

#### SAVORY

Savory, or "Summer Savory," is legally defined as the "dried leaf and flowering tops of *Satureja hortensis* L." and a tentative requirement of not more than 15 percent of stems, not more than 12 percent of total ash, nor more than 1.5 percent of acid-insoluble ash, has been fixed in S. R. A. No. 16, Item 162.

#### STAR ANISEED

This is the "dried fruit of *Illicium verum* Hook," containing "not more than 5 percent total ash."

#### TARRAGON

Tarragon, much used in flavoring vinegar (in some localities), is defined in the Federal standards as "the dried leaves and flowering tops of *Artemisia dracunculus* L.

#### THYME

This somewhat well known spice is defined in the Federal food standards as "the dried leaves and flowering tops of *Thymus vulgaris* L." containing "not more than fourteen percent (14%) total ash, nor more than 4 percent of ash insoluble in hydrochloric acid." Another official requirement (S. R. A. No. 14, Item 135) is that the stems (including petioles) and foreign matter shall not exceed 15 percent and the volatile ether extract ("ethereal oil") shall not be less than 1 percent.

The National Formulary, or drug law standard, defines thyme as the "tops of *Thymus vulgaris* collected when in flower" and containing "not more than 14 percent total ash."

#### TURMERIC OR CURCUMA

This spice, much used also as a coloring matter, is legally defined as "the dried rhizome or bulbous roots of *Curcuma longa* L." It is a principal ingredient of curry powder and analyzes as shown in Table 76. (See next page.)

Table 76. Analyses of Turmeric.

	Percent		
	Minimum	Maximum	Average
Moisture .....	8.07	9.08	8.73
Starch .....	29.56	40.05	34.21
Crude fiber .....	4.45	5.84	5.37
"Protein" (N x 6.25) .....	6.06	10.81	8.88
Volatile ether extract .....	2.01	4.42	3.19
Non-volatile ether extract .....	7.51	8.84	7.98
Alcohol extract .....	4.37	9.22	6.96
Total ash .....	5.99	8.52	7.07
Water soluble ash .....	4.74	6.14	5.36

Turmeric is not subject to adulteration. The coloring matter is known as curcumin.

#### WHITE PEPPER

As indicated in our remarks upon black pepper and as defined in the Federal food standards, white pepper is usually considered as the fully ripened berry of black pepper from which the outer shell or pericarp has been removed, leaving a grayish-white spherical berry, usually a trifle larger than black pepper berries, which, it will be remembered, are picked in an immature state.

Thus the Federal standard for white pepper reads as follows: "White pepper is the dried mature berry of *Piper nigrum* L., from which the outer coating or the outer and inner coatings have been removed and contains not less than seven (7) percent of non-volatile ether extract, not less than fifty-two (52) percent of starch, not more than three and five-tenths (3.5) percent of total ash, not more than three-tenths (0.3) percent of ash insoluble in hydrochloric acid, and not more than five (5) percent of crude fiber."

According to trade statements, however, not all white pepper is made from fully ripened berries. The manufacture of white pepper is a distinct and separate business, being frequently carried on at a distance from the plantation. The manufacturers buy the pepper in the open market, selecting what they consider suitable for their purpose, and generally with the understanding that the berries have been allowed to fully ripen. For example, in the manufacture of Penang white pepper the A grade of Acheen black pepper is preferred. The various varieties of white pepper correspond generally to the black peppers; thus we have Singapore, Tellichery, etc. Analytical data on six different varieties will be found in Table 77, on page 218.

The shells are removed by friction after soaking the pepper berries in water, after which the white pepper berries are often bleached.

Penang white pepper berries are often, if not usually, coated with a preparation of carbonate of lime. By cutting off from the end of each white pepper berry a piece of the outer skin a variety of white pepper, known as "Coriander," is prepared. Another variety is known as "Decorticated" white pepper, being that from which the seed coats have been entirely removed, forming smooth hard kernels. There are several grades of this variety depending upon to what extent the decorticating process has been carried. Thus we may find it with all three coatings removed, or only one or two of them. Ordinary white pepper has only the outer shell removed.

Ground white pepper should not, of course, have any different analytical makeup than the whole berry, unless it is allowed to take up considerable moisture. The following are the chemical results from samples of known purity, mainly those examined in the Connecticut and Michigan food inspection laboratories. The significance of most of the analytical items is no doubt familiar to most of our readers, by this time.

It will be seen immediately that in Table 77, determined upon samples of known purity and by the official testing methods called for in the Federal food law regulations, there are a number of items which decidedly transgress the Federal standard for white pepper. More than that, while in two instances (total ash and starch) there were only one or two samples, out of the thirty-four reported upon, that were off; in the case of the non-volatile ether extract nine were deficient and in crude fiber five excessive.

In every case the majority of samples that transgressed one or more limits (often several of them) were of the variety known as Penang. Penang white pepper, as said above, is usually made from matured Acheen A black pepper and by reference to our remarks and data on the Acheen peppers under the topic "Black Pepper," it will be readily understood how it is that Penang white pepper so often disagrees with the Federal white pepper standard. Yet in both the non-volatile ether extract and crude fiber certain samples of pure Singapore, Siam and even "Decorticated" white pepper transgress the standard.

Such facts as the above demonstrate decisively that the Federal standard for white pepper is in need of further revision, more so than the various other spice standards.

Ground and even whole white pepper is adulterated. Small wild peas and other spherical berries have been found in the whole white pepper, while cereal products, ground olive stones, ground bleached nut shells and ground leguminous products have been found in the



Table 77. Analyses of White Peppers.

Variety, etc.	Moisture	Percent						Weight in Grams per 100 Berries	
		Volatile Ether Extract	Non-volatile Ether Extract	Starch (Diastase Method)	Crude Fiber	Parts Nitrogen in 100 Parts Non-volatile Extract	Total Ash (Mineral Residue)		Ash Insoluble in Hydrochloric Acid
<i>Singapore</i> (9 Samples)—									
Minimum	8.15	0.90	5.68	53.11	3.39	4.22	0.94	0.06	4.35
Maximum	13.82	1.66	7.94	59.34	6.10	4.35	1.61	0.20	5.20
<i>Penang</i> (10 Samples)—									
Minimum	8.04	0.62	5.65	48.88	3.70	3.21	2.15	0.05	4.79
Maximum	14.19	1.64	8.65	54.74	7.65	4.37	4.28	0.41	5.62
<i>Siam</i> (5 Samples)—									
Minimum	8.66	0.58	5.71	55.01	3.49	4.20	1.26	0.04	4.49
Maximum	14.47	1.37	6.81	56.33	3.91	4.48	1.77	0.22	5.48
<i>Tellichery</i> (1 Sample)	10.49	1.15	6.09	57.09	3.39	4.31	0.86	0.07	5.40
<i>Decorticated</i> (8 Samples)—									
Minimum	8.14	0.49	5.96	57.38	0.10	4.23	1.00	0.00	2.56
Maximum	13.34	1.50	7.53	63.60	2.07	4.53	2.24	0.15	3.47
<i>Coriander</i> (1 Sample)	10.22	0.85	6.48	56.60	4.14	4.15	1.03	0.05	4.22

ground pepper. One of the first samples condemned in connection with the enforcement of the Federal Food and Drugs Act was a sample of white pepper evidently ground from whole berries accidentally contaminated with a small number of some species of small wild pea. The Federal duplicate with seals intact, analyzed by the author, using the official testing methods, was entirely normal and agreed throughout with the Federal standard. The microscope, however, plainly showed the presence of the small proportion of foreign starch granules resulting from the evident contamination of the whole white pepper with peas.

### LONG PEPPER

In the Federal spice standards, long pepper is defined as the "dried fruit of *Piper longum* L." It has been more usually included under the genus *Chavica*, Miq., two species of which, viz., *Chavica officinarum* and *Chavica Roxburghii*, constitute the more common forms. The latter grows wild along the river banks of India, the fruit appearing as cylindrical spikes from two to three cm. long, covered with closely packed coalesced berries, the whole being about the same diameter as a true pepper berry.

Similar to true pepper, long pepper contains the alkaloid piperin (about one-half as much as the average black pepper), starch, somewhat less fiber than black pepper, and resin. It has a peculiar and disagreeable odor, particularly when warmed, a fact which interferes with its use as an adulterant for true pepper. The starch granules of long pepper closely resemble those of white pepper under the microscope, the trifle larger size and greater angularity being only noticeable when the two are directly compared. With polarized light a surer differentiation is possible, and by spreading out in a thin layer on paper the pepper suspected of being adulterated with ground long pepper, and tapping from below, the bits of fluffy fiber coming from the central part of the catkin separate out and can be easily seen with a magnifying glass.

From its method of growth long pepper fruit often trails on the ground, and as the surface of the spikes is rough and indented, it frequently happens that long pepper contains a considerable proportion of dirt, clay, sand, etc., yielding a rather high ash figure upon analysis.

Table 78 shows the analytical limits obtained in the analysis of seven samples of long pepper, the data given being those determined by the official analytical methods only, similar to all analyses given in this series of articles on the Federal spice standards.

Table 78. Analyses of Long Pepper.

	Percent	
	<i>Minimum</i>	<i>Maximum</i>
Moisture .....	8.43	10.13
Volatile ether extract .....	0.79	1.55
Non-volatile ether extract .....	5.71	7.53
Starch (diastase method) .....	28.43	45.87
Crude fiber .....	5.76	10.01
Total ash .....	5.93	14.39
Ash insoluble in acid .....	0.22	5.92
Parts nitrogen in 100 parts non-volatile ether extract.....	3.12	3.56

The principal differences to be noticed between these analytical data and those for black pepper are the tendency towards a lower non-volatile ether extract figure (indicating less piperin), a generally higher total and acid-insoluble ash (due to extraneous dirt, etc.), and, rather strange to say, a noticeably lower crude fiber figure, averaging about two-thirds that of black pepper.

Long pepper is used whole to some extent in pickles and is naturally not subject to any adulteration, being itself usually considered an adulterant only for true pepper.

#### SCIENTIFIC SPICE BUYING

Experienced men in the spice trade have pretty definite and well founded views as to the relative values of the different varieties of a spice, and to a certain extent the value of fresh ground products as compared with old. But taking a given variety of a spice, or for that matter two varieties not decidedly inferior one to the other, is there sufficient appreciation of the exact, scientifically measurable values of spices as flavoring substances, for flavoring substances they should be, not merely powdered roots, berries and herbs such as a druggist deals in?

No baker, pickler or housewife buys spices as a filling material, for starch is much cheaper. Spices are bought, especially by manufacturers of food products, solely for a definite amount of a given flavor, supposed to be furnished by the spice in question. Whether a given quantity will impart flavor to one hundred pounds of dough or three hundred pounds is purely a business proposition, a question of factory costs.

That this is at last being recognized by a number of the largest biscuit and pickling concerns is attested to by a number of recent trade disputes, coming to the author for referee settlement. At last the analytical items known as "volatile ether extract" and "alcohol extract," comprehending the essential oils and resins present in spices,

are receiving considerable attention, and several disputes, caused in part by careless analytical determinations by inexperienced spice chemists, have gone to an unfortunate degree of accusation.

Such concerns as referred to above are now purchasing all spices upon analysis, paying particular attention to the essential oil and resin contents. Unground spices vary considerably in their content of flavoring constituents, and as the essential oils, after liberation from their cells by grinding, are volatile, it follows that of two samples of the same kind and variety of spice one may have several times the flavoring power of the other and be worth just so much more. More or less exhausted spices can be detected by taste, but the valuation of spices as referred to above can only be decided by chemical tests.

Unfortunately, hitherto the methods, even the official method, of estimating the "volatile ether extract" (essential oil) of a spice have been faulty and the results untrustworthy. The official method consists of extracting the finely-ground spice with absolute ether, allowing the ether solution to evaporate spontaneously (during which operation much water may be absorbed by the extract) and then drying in a closed dish over oil of vitriol for eighteen hours. The so-called "total ether extract" is thus obtained, and after heating this for a number of hours in an oven at certain temperatures the "non-volatile ether extract" remains. The difference between the "total ether extract" and the "non-volatile ether extract" is taken as the measure of the "volatile ether extract" or essential oil.

This method is quite faulty and seldom gives concordant results. By noticing the darkening of the oil of vitriol, especially the top layer, it becomes evident that more or less of the volatile essential oil has been absorbed and therefore lost, possibly carried along by the water vapor which has been attracted and absorbed during the slow evaporation of the ether, and is later attracted to and absorbed by the oil of vitriol. Also, of course, more or less loss of volatile oil occurs during the slow spontaneous evaporation of the ether itself.

Hortvet and West (*Journal of Industrial and Engineering Chemistry*, February, 1909), in their study of methods for estimating essential oils in flavoring extracts, have shown that an ethereal solution of an essential oil can be rapidly evaporated over a hot-water bath, with practically no loss of the oil and with complete removal of the ether and traces of alcohol vapor. For fifteen years, therefore, the author has been modifying the official method described above by quickly distilling off the ether, cooling the "total ether extract" in a desiccator for a few moments and immediately weighing. Then the volatile oil is

driven off in the oven as usual, the "non-volatile ether extract" weighed and the "volatile ether extract" obtained by difference.

The author has not had the time to make the desirable number of exact comparisons of the two methods that he would like to present as data and proofs, but he is very well satisfied that a much truer and higher valuation of the essential oil content of a spice is thus possible, which in the case of analyses using but a couple of grams of sample (and therefore subject to a big multiplication of errors) has amounted to several percents (on fresh ground mace, for instance), and has straightened out serious trade disputes.

If reliable determinations of essential oils in spices are therefore possible, it stands to reason that the valuation of spices on such a basis (or on the basis of "alcohol extract" in some spices, ginger, for instance) must be considered by the big buyers, who are purchasing simply for flavoring value.

Practically all published analyses of spices are of products which have been ground for some time. It would be of interest to secure data obtained, say, by the author's modification of the official method, on the essential oil content of spices at the moment of grinding. Such data would possibly form a basis whereby the length of time since grinding could be approximately judged on ground spices as sold in stores. It is hardly legitimate that spices so old as to have lost nearly all flavoring value should be sold, any more than spices exhausted by extraction of essential oil.

In some recent trade disputes there was a complaint that the moisture (water) content of the shipment was too high. This was found to be due to the use of the analytical method, giving too low a value for the "volatile ether extract," as it is customary to simply dry the sample in an oven at the temperature of boiling water and subtract the percent of "volatile ether extract" to get the percent of "moisture." The use of the author's method showed that not only was the moisture content normal, but that the shipment was extra good as concerns essential oil content.

The "volatile ether extract" content of mace has been considerably understated in published analyses, due to the above and possibly another cause. To drive off in an oven all the volatile ether extract of certain maces requires several days, and many times probably a low volatile and correspondingly unfairly high non-volatile ether extract (suggesting Bombay mace) has been thus reported. Recent cases in the author's practice involved differences of four and five percent,

causing pure samples to violate the 30 percent limit of the Federal standard for mace.

If better methods were in official use there is good cause for raising the volatile ether extract limit for cloves in the Federal standard, thereby restricting the occasional use of a certain added proportion of cloves exhausted of their clove oil.

## Chapter VIII.

### The Legal Chemistry of Maple Products.

The three principal maple products of commercial value are maple sap syrup, maple sugar or maple concrete, and maple sugar syrup. Under the common term "maple syrup" can be sold and is sold either maple sap syrup, maple sugar syrup or a mixture of the two.

Maple sap syrup was formerly the commonest form of "maple syrup" and represented the product obtained by boiling down (evaporating) maple sap to a desirable consistency, i.e., to that point where a cold gallon (231 cubic inches) weighed 11 pounds. The sap itself is obtained by boring a shallow hole (1 to 3 inches deep) three-eighths to one-half inch in diameter, into certain varieties of the maple tree (especially *Acer saccharum* and *Acer saccharum nigrum*), during late winter and early spring, so as to get the first flow of sap. Sap collected later, while the buds are opening, has an inferior flavor, due to fermentation by microorganisms and is described as "buddy." The sap is collected through a small inserted spout emptying into a pail hung beneath and is then carried to the evaporating camp or factory nearby. The hole must be kept clean by reaming out once or twice during the season, and the spouts and pails must be frequently cleaned, otherwise microorganisms collect, which, infecting the originally sterile sap, will cause color changes and a "souring" of the sap and later development of "off" flavors, including the "buddy" flavor.

The Vermont Experiment Station has carried on many investigations of the process and the products. Unpublished data determined by Dr. C. H. Jones of the Station shows the sap to have the composition shown in Table 79.

Table 79. Analyses of Maple Sap (10 samples).

	Percent		
	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Total solids .....	2.28	6.16	4.34
Sucrose (sugar) .....	2.14	5.53	3.94
Ash (residue after incineration) .....	0.035	0.103	0.062
Undetermined (malic acid, protein, etc.) ....	0.09	0.65	0.34

Sap obtained with precautions showed from 0 to 500 microörganisms per cubic centimeter; sap as ordinarily collected from 140 to 1,000,000; "sour" sap from 1,300,000 to 87,750,000, due to infection by foul spouts and dirty pails.

As stated above the original form of "maple syrup" was the maple sap syrup. Inasmuch as the evaporation of the sap to a thin syrupy consistency will drive off less of the volatile flavoring constituents than will evaporation to a solid sugar, we find that the sap syrups have a finer and more delicate flavor than the "maple syrup" made by dissolving maple sugar or concrete in water. The latter is a legal product under the title "maple syrup," but will analyze differently because of the precipitation of malic acid salts and other substances during the longer evaporation of the sap to syrup of sugar density and also because of filtering and other clarifying operations upon the redissolved sugar or concrete. It should be labeled as "maple sugar syrup" to distinguish it from the maple sap syrup.

It is somewhat interesting that maple sap contains the same acid (malic) as is found in the apple and several other fruits. The precipitated matter found in the bottom of the kettle or pan, after the heavy syrup is drawn off for sale as commercial maple syrup, is known as "niter" and is mainly a calcium malate mixed with sucrose and reducing sugars. Table 80 is interesting as showing how concentration of the thin syrup to a heavy syrup lowers (by precipitation) the content of malic acid and mineral matter as represented by the total ash and the insoluble ash.

Table 80. Effect of Concentration on Maple Sap Syrup \* (Jones).

	<i>Malic Acid Value</i>	Percent		
		<i>Total Ash</i>	<i>Soluble Ash</i>	<i>Insoluble Ash</i>
Average of 84 syrups (over 34% water)....	1.00	1.02	0.45	0.57
" " 42 " (30 to 34% water)....	0.71	0.80	0.48	0.32
" " 25 " (under 30% water)...	0.66	0.77	0.49	0.28

\* Calculated to a water-free basis.

The lowest values reached were 0.59 for total ash, 0.29 for soluble ash, 0.20 for insoluble ash and 0.44 for malic acid value. Some of these were obviously abnormal products and others, by diluting, warming, settling, decanting and then concentrating to standard consistency, were restored to a more normal analytical make-up, indicating that this procedure is desirable when analyzing a sap syrup of less than 32% water content.

From the above it will be readily seen how a "maple syrup" made



by dissolving maple sugar shows much less malic acid, total ash and insoluble ash than does a maple sap syrup concentrated to the maximum water content of 35 percent allowed in the Federal standard. This newer product, i.e., "maple sugar syrup," is now largely superseding the maple sap syrup, commercially, due to the saving in freight charges for a nearly water-free sugar as compared with a syrup containing 35 percent of water. Practically all the "compound" maple syrups, so largely sold in city stores, are mixtures of cane sugar (rock candy) syrup and "maple sugar syrup" and the official analyst is frequently called upon to judge the percent of maple product present, from a study of the ash, malic acid and "lead number" values. The "lead number" is a measure of the amount of basic lead acetate used in precipitating various substances from maple sugar solutions (including maple sap syrup) that are thus precipitated. It has become an important index in the analysis of maple products (also in vanilla extracts), as the commonest adulterants of both maple and vanilla bean products yield no "lead number." There are two methods of estimating and reporting the "lead number," viz.: the "Winton" (A.O.A.C.) and the "Canadian." The same conditions, during concentration of the sap to sugar density, that reduce the malic acid and ash values also reduce the "lead number," and unless the analyst knows that he is dealing with a product containing sap syrup he should not judge by the data given in Table 81 for maple sap syrups. For sap syrups, as they vary (slightly) in different localities, the reader should consult Bulletin 134 of the U. S. Bureau of Chemistry, from which most of the general data given in the table is compiled.

Table 81. Analyses of Maple Sap Syrups (481 samples).

	Percent		
	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Moisture (water and volatile esters) . . . . .	24.85	48.14	34.22
Sucrose (Clerget method) . . . . .	47.20	70.46	62.57
Invert sugar (copper reduction method) . . .	0.00	11.01	1.47
Total ash (residue from mineral salts) . . . .	0.45	1.06	0.66
Undetermined (malic acid, tannin, etc.) . . . .	0.00	4.51	1.08
Direct polarization (normal weight) . . . . .	+42.10°V.	+69.00°V.	+60.64°V.
Invert polarization (at 20° C.) . . . . .	-17.00°V.	-24.97°V.	-22.34°V.
"                    "                    (at 87° C.) . . . . .	+ 0.60°V.	- 2.40°V.	0.00°V.

The invert sugar results from the action of malic acid (and traces of other acids) upon sucrose during the concentration of the sap and storage of the syrup, as the sap itself seldom if ever contains any. That this change continues during storage is evidenced by the analysis

(by the author) of a maple syrup which had stood in a warm laboratory for 15 years and which showed nearly half of the sucrose to be inverted into invert sugar. Fermentation also will result in the formation of invert sugar.

The invert polarization at 87° C. is for the purpose of detecting any commercial glucose (starch syrup or starch sugar), as at 87° C. the invert sugar is optically inactive and the strong dextrorotatory power of the dextrin of commercial glucose manifests itself. Only two of the 481 samples of pure maple sap syrups represented above showed a dextrorotatory reading (very slight) at 87° C., due to natural causes.

The sap syrup will show little or none of the protein which is present in the sap itself, as this, together with traces of other organic material, is coagulated during the evaporation and is skimmed off.

The data on the ash, malic acid value and lead number are usually calculated to a uniform moisture-free basis for all maple products. In Table 82 these data are given for the 481 pure maple sap syrups reported above:

Table 82. Ash, Lead Number and Malic Acid Determinations on Maple Sap Syrups (481 samples).

(Calculated to a moisture-free basis.)

	Percent		
	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Total ash (residue from mineral salts) .....	0.68	1.68	1.00
Soluble ash .....	0.35	1.23	0.63
Insoluble ash .....	0.23	1.01	0.37
Ratio insol. ash to soluble ash .....	0.53	3.86	1.70
Alkalinity of soluble ash (cc. N/10 acid per 100 gr.)	41.0 cc.	122.0 cc.	75.0 cc.
Alkalinity of insoluble ash (cc. N/10 acid per 100 gr.)	41.0 cc.	208.0 cc.	97.0 cc.
Ratio insol. ash alkalinity to soluble ash alkalinity	0.21	1.83	0.77
Winton lead number (A.O.A.C. method) .....	1.76	4.41	2.70
Canadian lead number (on 454 Canadian syrups)	1.51	5.66	3.12
Malic acid value (Cowle's method) .....	0.21	1.82	1.01

Presumably some of the Canadian syrups were maple sugar syrups in which material precipitated by lead subacetate had been lost in the evaporation to form maple sugar or concrete or in filtrations of the redissolved sugar. The sugar would be mixed more or less with precipitated salts, etc., and although analyzing legal for Canadian maple sugar, a filtered solution of it would show decidedly less of said salts. Therefore it is probable that the minimum for Canadian lead

number on a maple sap syrup would be above 2 on the moisture-free basis.

In Table 79 at the beginning of this chapter are given the range of composition and average values for ten samples of pure maple sap. The average values calculated to a moisture-free basis, as above, are given below, by courtesy of Dr. C. H. Jones:

	Percent
Sucrose .....	90.78
Total ash .....	1.42
Undetermined matter .....	7.80

Comparing the above total ash with the average for maple sap syrups, i.e., 1.00 percent on a moisture-free basis, it will be seen that during the evaporation necessary to get a thin syrup there is a considerable loss of mineral salts (mainly calcium malate) by precipitation. As the evaporation continues the loss is increased somewhat (maple sugars average 0.95 percent total ash on a moisture-free basis), but the greater part of the loss is during the earlier stages of evaporation.

In the above analyses of maple sap syrup, the average value for "undetermined matter" is 1.08 percent. The maple sap data gave an average value (0.34 percent) which figured out to a maple sap syrup of legal density shows 5.07 percent as the amount to be expected in the syrup. That this is not attained is due to the fact most of it coagulates during evaporation and is removed by skimming.

In the manufacture of maple sugar, it is the practice, except when making fancy cake sugar, to incorporate the skimmings and settlings (precipitated "niter"), and samples have been found with a total ash value of 3.0 percent! For proper analysis the sugar should first be redissolved and filtered free from coagulated and precipitated matter.

There are various commercial grades of maple sugar, such as "hard" sugar, "soft" sugar, "stirred" or "grained" sugar, "cake" sugar and "tub" sugar. "Hard" sugar is difficult to break when in cake form; "soft" sugar is that which in cake form is easily broken. "Stirred" or "grain" sugar is stirred during cooling and crystallization and resembles commercial brown sugar. "Tub" sugar is a soft sugar, often in a "mushy" condition, in which more or less mother liquor has drained off to the bottom of the tub or other container.

"Hard" sugar contains less moisture than "soft" sugar due to longer boiling. The data in Table 83 show how the moisture content varies in different grades of maple sugar.

Table 83. Moisture Content of Maple Sugars (Bryan).

	Percent
Very dry "grain" sugar .....	0.65
Medium dry "grain" sugar .....	3.84 to 8.42
Soft "grain" sugar .....	11.00
Very hard "cake" sugar .....	1.43
Hard "cake" sugars .....	2.10 to 8.18
Medium hard "cake" sugars.....	5.53 to 9.67
Soft "cake" sugars .....	9.64 to 11.20

As low as 0.06 percent and as high as 15.67 percent moisture have been reported in maple sugars, but the average sugar has less than 8 percent moisture.

The Federal standard for maple sugar or maple concrete does not fix any analytical limits, merely defining it as "the solid product resulting from the evaporation of maple sap or maple syrup." Maple syrup is defined as "syrup made by the evaporation of maple sap or by the solution of maple concrete, which contains not more than thirty-five percent (35%) of water and weighs not less than eleven (11) pounds to the gallon (231 cu. in.)."

In Bulletin 466 of the U. S. Department of Agriculture are reported analyses of 363 samples of maple sugar made in eleven different states and seven Canadian districts. For variations in different localities the above bulletin should be consulted. Below are given the data on all of the 363 samples, calculated to a moisture-free basis:

Table 84. Analyses of Maple Sugars (363 samples).\*

(Calculated to a moisture-free basis.)

	Percent		
	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>
Sucrose (Clerget method) .....	57.04	98.62	90.69
Invert sugar (copper reduction method) .....	0.00	35.26	6.19
Undetermined (malic acid, gums, protein, etc.) .....	0.00	8.18	2.14
Total ash (residue from mineral salts) .....	0.76	1.70	0.95
Soluble ash .....	0.30	1.14	0.60
Insoluble ash .....	0.21	1.00	0.35
Ratio insol. ash to soluble ash .....	0.43	4.07	1.69
Alkalinity of soluble ash (cc. N/10 acid per 100 gr.) .....	42.0 cc.	140.0 cc.	75.0 cc.
Alkalinity of insoluble ash (cc. N/10 acid per 100 gr.) .....	31.0 cc.	190.0 cc.	87.0 cc.
Ratio insol. ash alkalinity to soluble ash alkalinity .....	0.37	2.29	0.86
Winton lead number (A.O.A.C. method) .....	1.85	4.95	2.76
Malic acid value (Cowle's method) .....	0.51	1.72	0.93

\* U. S. Dept. Agriculture Bull. 466.

The data on "undetermined" average about one-fourth the average for maple sap, calculated to a moisture-free basis. This is due to the sugar having been dissolved and filtered before analysis. For the same reason the average ash content (i.e., 0.95 percent) is considerably less than that of maple sap calculated to a moisture-free basis.

The composition of the ash of maple sap and maple syrup is of interest, and the following recalculated data, reported in Bulletin 134 of the U. S. Bureau of Chemistry, give the range of constituents, together with certain characteristic ratios:

Table 85. Average Composition of Ash of Maple Sap and Maple Syrup.\*

	Percent	
	Maple Saps (7)	Maple Syrups (100)
Potassium ( $K_2O$ ) .....	40.32	38.07
Sodium ( $Na_2O$ ) .....	2.09	....
Calcium ( $CaO$ ) .....	30.81	21.88
Magnesium ( $MgO$ ) .....	9.09	....
Iron ( $Fe_2O_3$ ) .....	1.34	....
Phosphoric acid ( $P_2O_5$ ) .....	9.68	5.39
Sulfates ( $SO_3$ ) .....	....	1.59
$K_2O/CaO \times 100$ .....	151.6	174.0
$P_2O_5/CaO \times 100$ .....	33.7	24.0
$SO_3/CaO \times 100$ .....	....	7.0
$SO_3/K_2O \times 100$ .....	....	4.0

\* U. S. Bur. Chem. Bull. 134.

It is of interest to note that the principal change from sap to syrup is a loss of calcium and phosphoric acid. As stated above, the precipitated "niter," found in the bottom of the kettle or pan used for concentrating sap to syrup, is mainly calcium malate. More complete analysis might probably show some calcium phosphate also, or it may be that the coagulated "skimmings" contain an appreciable proportion of phosphorus.

A very large proportion of the maple sugar manufactured is used in the preparation of maple sugar syrup, which, as stated before, is legally allowed to be sold as "maple syrup" and which is used also in large quantities for flavoring cane sugar (rock candy) syrups for the cheaper trade. Determination of the proportion of maple sugar or maple sugar syrup in the latter mixtures requires careful analytical work and a knowledge of how the maple sugar syrup is affected by redissolving the sugar or concrete and clarifying and filtering from suspended matter.

In Bulletin 466 of the Bureau of Chemistry (page 38) are given some data on maple sap syrups and also on the maple sugar syrups

made by boiling down these sap syrups to a solid sugar, redissolving to standard consistency and filtering. Table 86, with results calculated to a moisture-free basis, shows a distinct reduction in total ash, insoluble ash, Winton lead number and Cowle's malic acid value, to have taken place.

Table 86. Changes from Maple Sap Syrup to Maple Sugar Syrup.\*  
(Moisture-free basis)

	Percent	
	<i>Average of 10 Sap Syrups</i>	<i>Sugar Syrups from Same</i>
Sucrose .....	95.12	93.95
Invert sugar .....	1.48	2.56
Total ash .....	0.87	0.81
Insoluble ash .....	0.31	0.24
Winton lead number .....	2.39	2.11
Malic acid value .....	0.86	0.65

\* U. S. Bur. Chem. Bull. 466.

These results show that a further precipitation of calcium malate occurs during the boiling down to form maple sugar and that one can not judge maple sugar syrups by maple sap syrup data. Moreover, the grade of maple sugar prepared for the maple sugar syrup trade is very inferior to the maple sugar prepared as above or sold as a confection. Little care is taken in its manufacture in the woods and much of it is very dark colored, sticky and strong in flavor. Considerable treatment with filtering aids (kieselguhr, etc.) is necessary for clarifying it after redissolving. Some recent data by Lancaster of the Canadian Department of Health show distinctly less total ash and lead number values, after full manufacturing treatment, than in the original sugar solution before adding kieselguhr and filtering. In three experimental batches the total ash showed an average decrease of 0.19 percent and the Canadian lead number an average decrease of 0.28 (maximum decrease was 0.42), when all results were calculated to a moisture-free basis. The author called attention to these points in a Federal food inspection case many years ago, where a "compound" syrup, known to contain 25 percent of maple sugar syrup was alleged to contain less than 10 percent. The prosecution was dropped, as the data on the sample had been judged by data on maple sap syrups, by the Government experts. Many more data on maple sugar syrups (calculated to a moisture-free basis), than we have, are desirable.

As to the adulteration of maple products, by far the commonest adulterant is ordinary refined cane or beet sugar. This, having little or no ash, no malic acid value and practically no lead number, acts

merely as a diluent to reduce those items in maple products. Somewhat shrewder is the use of various grades of raw, brown and Muscovado sugar, the latter being mainly detectable by the fact that its ash is higher in sulfates and phosphates and lower in calcium than the ash of maple products. The data in Table 87 are of value for analytical comparisons.

Table 87. Ash Data on Adulterants of Maple Products.

	Percent			Alkalinity	Alkalinity	Ratio	Insol.
	Total Ash	Soluble Ash	Insol. Ash	of Soluble Ash (cc. N/10 Acid)	of Insol. Ash (cc. N/10 Acid)		
Brown sugars...	0.51 to 4.33	0.44 to 2.74	0.06 to 1.59	15. to 76.	15. to 234.	1.7 to 16.7	
Raw cane sugars	0.32 to 0.59	0.10 to 0.41	0.18 to 0.23	18. to 36.	42. to 52.	0.5 to 2.3	
Beet sugars.....	0.33 to 0.86	0.31 to 0.78	0.02 to 0.08	38. to 40.	2. to 28.	9.8 to 15.5	
Muscovado.....	1.30 to 1.33	1.18	0.12	11.	3.	7.7	

The Winton lead number of the Muscovado sugars averaged 2.10 and the malic acid value 1.21.

The analytical limits which have been proposed for judging the purity of all maple products are: On a moisture-free basis, Total ash not less than 0.77 percent, Insoluble ash not less than 0.23 percent, Winton lead number not less than 1.85 and Malic acid value not less than 0.60.

## Appendix A.

### AMENDED STANDARDS AND DEFINITIONS FOR FRUIT AND FRUIT PRODUCTS

As a guidance for officials of the department in enforcing the Federal Food and Drugs Act the Secretary of Agriculture, upon the recommendation of the Food Standards Committee, has adopted revised and amended standards and definitions for fruit and certain fruit products. The Food Standards Committee is composed of representatives of the Association of American Dairy, Food and Drug Officials, of the Association of Official Agricultural Chemists and of the United States Department of Agriculture.

The complete text of the revised definitions and standards follows:

1. **FRUIT** is the clean, sound, edible, fleshy fructification of a plant and is characterized by its sweet, acid, and/or ethereal flavor.

2. **FRESH FRUIT** is fruit which has undergone no material change other than ripening since the time of gathering.

3. **DRIED FRUIT** is the clean, sound product resulting from the evaporation of the greater portion of the water from properly prepared fresh fruit.

a. The term "sundried" is commonly used to designate the product dried without the use of artificial heat.

b. The terms "evaporated" and "dehydrated" are commonly used to designate the product dried by the use of artificial heat.

4. **"COLD-PACK" FRUIT** is the clean, sound product obtained by packing, in a suitable container, properly prepared fresh fruit, with or without the addition of sugar (sucrose), and maintaining it at a temperature sufficiently low to insure its preservation.

5. **CANNED FRUIT** is the clean, sound product made from properly prepared fresh fruit, with or without water and/or sugar (sucrose)

a. by processing in a suitable, hermetically sealed container, or  
b. by heating and packing in a suitable container which is then hermetically sealed.

6. **PRESERVE, FRUIT PRESERVE, JAM, FRUIT JAM**, is the clean, sound product made by cooking to a suitable consistency properly prepared fresh fruit, "cold-pack" fruit, canned fruit, or a mixture of two or of all of these, with sugar (sucrose) or with sugar and water.



In its preparation not less than forty-five (45) pounds of fruit are used to each fifty-five (55) pounds of sugar (sucrose).

A product in which the fruit is whole or in relatively large pieces is customarily designated a "preserve" rather than a "jam."

7. **GLUCOSE FRUIT PRESERVE, CORN SYRUP FRUIT PRESERVE, GLUCOSE FRUIT JAM, CORN SYRUP FRUIT JAM**, is the clean, sound product made by cooking to a suitable consistency properly prepared fresh fruit, "cold-pack" fruit, canned fruit, or a mixture of two or of all of these, with glucose, or corn syrup. In its preparation not less than forty-five (45) pounds of fruit are used to each fifty-five (55) pounds of glucose, or corn syrup.

8. **FRUIT BUTTER** is the sound product made from fruit juice and clean, sound, properly matured and prepared fruit, evaporated to a semi-solid mass of homogeneous consistency, with or without the addition of sugar and spices or vinegar, and conforms in name to the fruit used in its preparation.

9. **GLUCOSE FRUIT BUTTER, CORN SYRUP FRUIT BUTTER**, is a fruit butter in which glucose, or corn syrup, is used in place of sugar (sucrose).

10. **JELLY, FRUIT JELLY**, is the clean, sound, semi-solid, gelatinous product made by concentrating to a suitable consistency the strained juice, or the strained water-extract, from fresh fruit, from "cold-pack" fruit, from canned fruit, or from a mixture of two or of all of these, with sugar (sucrose).

11. **GLUCOSE FRUIT JELLY, CORN SYRUP FRUIT JELLY**, is the clean, sound, semi-solid, gelatinous product made by concentrating to a suitable consistency the strained juice, or the strained water-extract, from fresh fruit, from "cold-pack" fruit, from canned fruit, or from a mixture of two or of all of these with glucose, or corn syrup.

12. **CITRUS FRUIT MARMALADE** is the clean, sound, jelly-like product made from the properly prepared juice and peel, with or without the pulp, of fresh citrus fruit, of canned citrus fruit, or of a mixture of these, by cooking with water and sugar (sucrose). It contains, embedded in the mass, pieces of the fruit peel, with or without portions of the pulp of the fruit.

## Appendix B.

### HOW CARBONATED FRUIT BEVERAGES ARE MADE \*

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It is said that the training of a child should begin with his grandfather. For a first class fruit product, it is necessary to have fruit of good quality from which to produce it. The better the quality of the fruit the better will be the product made from it. This may not be evident in the finished product without a standard for comparison but I think we will all agree that a large, ripe, perfect fruit tastes better than a small, gnarly fruit of the same variety. Cultural methods and climatic conditions are factors which almost entirely control the quality of fruit.

Fruit which has been irrigated excessively late in the ripening period will be large and have juice with low sugar content and poorer flavor than fruit which has ripened with a less abundant supply of water. Fruit ripened where the water supply is very limited will be small with a high sugar content and rich flavor. Frost bitten fruit deteriorates rapidly and yields juice of inferior quality.

The question which naturally arises is "What is normal fruit of any given variety and what conditions are necessary for the best development of that fruit?"

Considerable work has been done on standardization of fruits so that with many of our fruits definite standards have been adopted by which the grade of any variety of fruit grown in a certain locality may be determined by comparison with this standard. Cultural methods which will produce fruit nearest to this standard should be adopted.

It is the desire of every fruit grower to produce perfect fruit only. In spite of all precaution which might be taken in cultural methods there will be some undergrade fruit. By undergrade, we mean slightly blemished, undersized, oversized or malformed though sound, fruit. Unsound fruit should never be used because it is impossible to obtain

\* Reprinted from *The Fruit Products Journal and American Vinegar Industry*, Nov., 1924.

a good product from bad fruit. Decayed or wormy fruit should never be used.

### Sorting

Means for proper sorting and inspection should be provided. Where fruit is delivered to the plant and used immediately this can be done in the field or orchard as a part of the regular grading operations. If fruit is to be stored and held for some time before using, an additional sorting will be necessary for the removal of fruit spoiled during storage.

### Washing

The importance of washing cannot be overemphasized. Besides the desire and necessity for a clean product, there is the facilitating of subsequent operations of filtration, clarification and preservation, all of which are accomplished more easily and more perfectly by having clean fruit. If fruit has been grown under especially favorable conditions away from dusty roads, free from smut, mildew, mold and other contamination and has been kept clean, washing may be dispensed with. Such conditions, however, are very rare.

Fruit of a hardy nature such as apples, citrus fruits, pomegranates, etc., which permit of rough handling may be washed by the washer in common use in the citrus packing houses for washing oranges and lemons.

The more perishable fruits such as grapes, berries, and cherries which will not stand such rough treatment should be washed by a machine with a spray system similar to that commonly used to wash tomatoes.

Berries and grapes grown by the dusty roadsides are very apt to be sandy and muddy or dusty. This dirt adheres to the rough surface and is difficult to remove except by washing.

For handling fruits on a small scale at home washing may be accomplished by using tubs and screen trays, both of which are easily available.

The operation of crushing varies greatly with the nature of the fruit and is accomplished for the purpose of releasing the juice more readily from the cells or juice sacs.

For the extraction of apple juice crushing is a very important operation. The machine commonly used for this purpose is called the apple grater or crusher. This machine varies in size from the small hand power size for home use or the orchard size for community use which may be operated by hand lever or by machine power,

to the large commercial size with a capacity of ten to thirty tons a day.

For the most efficient extraction of apple juice the fruit should be crushed to pieces  $\frac{1}{8}$  to  $\frac{1}{4}$  inch thick. The size of pieces can be regulated by adjustment of the rolls.

This grater or crusher consists of a steel cylinder from 6 to 8 inches in diameter on the surface of which is set a row of knives extending the full length of the cylinder. Parallel with the cylinder is a set of upright knives or a fluted steel plate towards which the cylinder revolves. The fruit in passing between these knives and cylinder is shredded or grated.

The apple grater may be adjusted to use in crushing grapes also. For crushing grapes and other soft fruits the roller crusher is in common use. In a modified form it is also used for crushing citrus fruits. It consists of two fluted cylinders which revolve towards each other. They are placed in the same plane in a horizontal position above which is a hopper. The fruit passes downward between the rolls and is crushed by pressure. When used for crushing grapes it may be attached to a stemmer by which the stems are removed from crushed grapes.

### Repressing

In the production of apple juice repressing is a very important step in the process. A 50 percent increase in yield is often obtained by this operation.

The pomace obtained by the first pressing is macerated by means of the pomace picker which grinds it to a meal-like consistency and is pressed again. The juice obtained by this second pressing has a darker color, a higher sugar content and more astringency than that from the first pressing. This is especially good for vinegar manufacture because of the high sugar content. It may be used also for blending with juice from the first pressing.

The increase in yield by use of the pomace picker and repressing will in a very short time pay for the machine and the extra expense of this operation. The continuous crusher and press type is especially suitable for crushing berries and cherries.

The pomegranate which is developing into an important juice fruit requires little or no crushing. Any operation which macerates the peel to extract an excess of the tannin is undesirable. Citrus fruits may be crushed by means of the roller crusher, where there is no objection to the extraction of the oil from the peel with the

juice. This oil may be separated from the juice subsequently by means of the cream separator.

Citrus fruit juice is commonly extracted by means of a conical spindle extractor in which case no crushing is required. For citrus fruits and other fruits with juices of similar character, pomegranates, all equipment with which the juice comes in contact should be made of non-corrodable metal such as silver, blocktin, monel metal, bronze or glass.

Juices coming in contact with iron, zinc, lead and other corrodable metals are impaired in color and flavor and may be injurious to the health.

### Heating

The main purposes of heating are to extract color, to increase yield and to facilitate filtration and clarification. The color element of many fruits is located in the skin. In order to liberate this color it is necessary to heat the fruit. Red grapes, berries and cherries are in this class. Apples, white grapes and other fruits, from which the juice is desired for flavor, are not heated before pressing.

It has been found that heating the crushed fruit to 160° F. is sufficient to liberate the color. Heating weakens the cell walls, causing a more complete release of the juice, thus giving a higher yield. Heating has a tendency to destroy the fresh flavor of the aromatic fruits such as the citrus, muscat and other flavor grapes. Heating coagulates the protein in fruit juices and facilitates filtration and renders permanent clarification possible.

If this heating is to a temperature equal to or greater than that of the final pasteurization temperature a permanently clear juice may be obtained. The coagulated protein is removed by filtration. If the final pasteurization temperature is higher a further coagulation of protein occurs which will appear as a cloud in the finished product.

There are two general types of presses in common use in the fruit juice industry, the "cloth and rack" type and the "basket" type. These designate the way the fruit pulp is handled. Other types are designated by the manner in which the pressure is applied in pressing, such as the beam press, screw press and hydraulic press, all of which are discontinuous. Another type is the continuous press into one end of which the fruit is fed, and to which pressure is applied. The pomace is discharged continuously at the opposite

end of the press while the juice passes through openings in the bottom. For apples and berries the rack and cloth type is most commonly used. A pressure of several hundred pounds per square inch is applied. The apple pomace, after the first pressing, is run through the pomace picker which grinds it up finely and is repressed. This repressing often results in a 50 percent increase in yield of juice.

There are small presses of both of the above types available for home use or for a small commercial scale production.

### Pressing of Pomegranates

Because of the peculiar nature of the pomegranate it requires different treatment than any other fruit. The color of the pomegranate is in the juice, therefore, it does not require heating for the extraction of color. Because of the high tannic acid content of the peel it is not desirable to extract the juice from the peel. The less the peel is broken or crushed the less tannic acid there will be in the juice.

For a long time the greatest obstacle in the way of producing palatable beverages from pomegranates was the astringency due to an excess of tannic acid.

By crushing by ordinary machines for that purpose the peel was so macerated as to extract an excess of the tannic acid with the juice. It was found that the less the peel was macerated the less astringency there was in the juice. By pressing the whole fruit without previous crushing a minimum of tannic acid was obtained. In fact by those familiar with pomegranate juice, there was said to be a deficiency of astringency. The basket type press was found most satisfactory for this purpose. High pressure is necessary for efficient extraction.

### Filtration and Clarification

Filtration may be accomplished without producing clarification. This is especially true of apple juice and white grape juices. Solid particles may be removed by filtration through closely woven cloth, felt jelly bag or wood pulp, cotton pulp or paper pulp filters under pressure, while colloidal particles may remain, giving a cloudy appearance to the juice.

By using a clarifying agent such as infusorial earth or diatomaceous earth an apparently clear and sparkling juice can be obtained, but after standing several months there is a precipitate unless filtration is repeated several times.

By heating the juice the protein is coagulated. Then by the use of infusorial or diatomaceous earth a permanent clearness may be obtained. The use of these clarifying agents necessitates the use of a filter press, which consists of a series of plates either metal or wood between which are placed pieces of canvas on which the filter mass is formed. Each section consisting of a piece of canvas and two plates, acts as an independent filter although all are fed from one general source.

Filtering media which have been very satisfactory are an especially treated "Filter-Cel" and a baked diatomaceous earth known as "Diatomite."

For the clarification of grape juice it is necessary to allow the cream of tartar to precipitate out before filtration. If cold storage facilities are available this may be accomplished in a few days. Otherwise it might require several weeks.

After heating, berry, cherry and pomegranate juices may be filtered brilliantly clear without the use of a clarifying agent. It is claimed by some that the cloud present in juice is an indication that it is pure fruit. If it is brilliantly clear it is thought that too much of the real fruit elements has been removed.

This is especially true of orange juice. The more pulp of the orange that can be held in suspension in the juice the better it is. The popular idea of grape juice also seems to favor the cloudy type like Welch's. It has been found that brilliantly clear juice can be produced from strawberries, blackberries, loganberries and pomegranates with no apparent loss of the real fruit constituents.

The simplest method of producing bottling syrups is by adding cane sugar to the clarified fruit juice. This is the method which we have used in making syrups from berries. The berry juices are of such low sugar content and high acid content that they require the addition of sugar to make a palatable drink.

### Concentrates for Beverages

The most economical form in which fruit juices can be handled in the production of beverages is in the form of concentrates. Concentration of fruit juices may be done in several ways with varying degrees of success. By open kettle method which is not conducive to retention of fresh fruit flavor and color. By concentration in vacuum which has proved satisfactory in concentrating orange and

lemon and grape juices which are now produced in commercial quantities, by this method.

Blackberries, cherries and pomegranates have been concentrated in vacuum successfully and give evidence of successful commercial products.

### Concentration by Freezing

This is a process which has been developed by Gore and Monti but has never been used extensively for commercial production. Experimental work carried on in conjunction with our laboratory work has developed a freezing process which is economical and practical. The freezing process ranks first of all concentration processes for quality of product. The aroma, flavor and color of the original juice are preserved perfectly.

### Syrups Made from Concentrates

These concentrates permit of various degrees of dilution, approximately as follows:

Orange, 1 part concentrate to 5 parts simple syrup.

Lemon, 1 part concentrate to 25 parts simple syrup.

Cherry, 1 part concentrate to 8 parts simple syrup.

Pomegranate, 1 part concentrate to 5 parts simple syrup.

A simple syrup of 60° is used.

Blackberry has not a very distinctive flavor so it is not desirable as a beverage by itself. It has a very deep permanent color.

Strawberry juice has a very strong flavor but a weak color. It has been found very satisfactory to blend the strawberry with blackberry which produces a very attractive beverage of a deep red color, having a very distinctive strawberry flavor. This is labeled "Strawberry with Blackberry."

From 1½ to 2 ounces of this syrup is added to a seven ounce bottle and filled with carbonated water.

### Carbonation

Carbonation increases the acidity of the beverage. Since most fruit juices have sufficient acid to make them palatable a low carbonation is usually necessary. This is especially true of orange. The optimum carbonation for orange beverage is the smallest possible to still have it perceptible. Strawberry and loganberry beverages permit a somewhat higher carbonation. Consumers' tastes vary greatly in this respect, however. Some prefer high carbonation, some



low and some none at all. The amount of carbonation then must be determined by the taste of the majority.

All carbonated fruit beverages require pasteurization for preservation. Carbonic acid gas is a preservative but it has not been found sufficiently effective as such in quantities so low as is required for making palatable carbonated fruit beverages.

It has been found that a temperature of 150° F. for 30 minutes is necessary for permanent preservation of 7 oz. bottles. Non-carbonated beverages in the same size bottles require from 165° F. to 175° F. for 30 minutes.

The presence of carbonic acid gas lowers the death temperature of mold spores. Commercial pasteurizers are available at bottling equipment supply houses, with capacities varying according to the requirements. On a small home scale, pasteurizing may be done by using a wash boiler or tin wash tub.

The sealed bottles are placed in the boiler which is filled with cold water. Heat is applied and the temperature of the water raised gradually to 150° F. The heat is then regulated to maintain that temperature for 30 minutes, at the end of which time it is turned off and cold water allowed to flow slowly into the pasteurizer and the hot water drained at the same rate, maintaining the original volume of water in the pasteurizer. Extreme care must be exercised not to allow the stream of cold water to come in contact with hot bottles or there will be breakage. This may be done by allowing the cold water to flow into a pan or other vessel submerged on top of the bottles. When the temperature of the bath has been reduced to between 110 and 120° F., the cold water may be turned off and the pasteurizer allowed to drain. The cooling may be completed in air.

There is a tendency for these beverages to deteriorate with age. For best results the orange beverages should be consumed within two months after production, otherwise a stale taste develops which is objectionable to many. Lemon will keep considerably longer than orange without any apparent deterioration. The color of strawberry beverages has a tendency to fade, especially when exposed to bright sunlight. When combined with blackberry this tendency is lessened, however. Loganberry has a more permanent color and flavor.

These beverages are rapidly growing in popularity and are attracting the attention of commercial bottlers in many parts of the country. The prospects are that in the near future these beverages will constitute a large proportion of the beverages consumed in this country.

## Appendix C.

### INVESTIGATION OF METHODS OF PREPARING CARBONATED BEVERAGES FROM FRUITS

Regarding the work done by Professors Cruess and Irish of the Agricultural Experiment Station of the University of California at Berkeley last year, the report of the experiment station follows:

"Syrups of 50° Balling were made from various fruits, namely, second-crop Muscat grapes, loganberries, Lawton blackberries, strawberries, Himalaya blackberries, raspberries and pomegranates. A 'fruit punch' syrup was prepared from red grape syrup, orange juice and lemon juice.

"The berry syrups were prepared as follows: The fruit was washed, crushed, heated to 150° F. and pressed. The juice so obtained was filtered and sugar was added to increase the density to 50° Balling. Muscat grapes were crushed and pressed and the juice was heated to 160° F. and filtered. Red wine grapes were crushed, heated to 160° F. and pressed and the juice filtered. The grape juices were concentrated in a glass-lined vacuum pan to 50° Balling. Pomegranates were cut in half and pressed in an apple cider press successfully. The juice was clarified by heating to 160° F., settling and filtering. Sufficient sugar was added to give a syrup of 50° Balling.

"Filtration through wood pulp gave better results than were obtained with a filter press and infusorial earth. Infusorial earth tended to impart a disagreeable 'earthy flavor' to the juices.

"Most of the syrups were held in cold storage; some lots at 0-15° F. and others at 32° F. Lacquered cans were used as containers. Other samples were pasteurized in lacquered cans or in bottles and held at room temperatures. Syrups stored in sealed containers at 0-15° F. retained perfectly their original color, flavor and aroma. Most of the samples held at 32° F. remained in good condition, although molding of the syrups occurred in a few of the containers (lacquered cans). Syrups pasteurized and stored at room temperature deteriorated slightly in color and flavor, but still produced very pleasing beverages when diluted with carbonated water.

"The fruit syrups were used in the preparation of carbonated bottled beverages for the purpose of demonstrating that attractive pure fruit drinks can be produced and sold at a moderate price to replace the synthetic imitation fruit beverages now sold.

"One and one-half ounces of the syrup per 7-ounce soda water bottle was used. Carbonated water was added to fill the bottles. These were capped and pasteurized in water at 150° F. for 30 minutes in most cases and were stored at room temperature. Most of the beverages have retained their flavor and color very satisfactorily for the duration of the storage period (eight months).

"Five hundred bottles of the beverages were offered for sale at the University Farm picnic on April 29. The bottles were chilled in ice water before sale. Ten cents per bottle was charged for the beverages. The entire lot was sold in about three hours, many of the sales being due to 'repeat orders.' Raspberry, strawberry, 'fruit punch' and Muscat red wine grape blend proved to be the most popular beverages. The pomegranate beverage was also much in demand. The beverages are now on sale in Berkeley and are being well received.

"The cost of production of the beverages from the berries is estimated at 3½¢ a bottle, exclusive of the bottle, and 6¢ a bottle if the cost of the bottle is included. This cost is based on a price of \$1.20 per gallon to the bottler for the syrup, or a gross return to the manufacturer of the syrup of about 80¢ per gallon.

"In experiments to determine the minimum safe pasteurizing temperatures for fruit beverages conducted by Cruess and Irish, it was found that although resistant mold spores and spore-bearing bacteria were not destroyed at 150° F., carbonated juices inoculated with yeasts; molds and spore-bearing bacteria and pasteurized at 150° F. for 40 minutes did not spoil, because the carbon dioxide prevented the growth of the heat-resistant organisms. This temperature and time of pasteurizing killed the yeast cells, the only one of these organisms capable of developing in the carbonated juice.

"Mold spores developed and caused spoiling of non-carbonated juice pasteurized 30 minutes at 170° F., but mold did not develop in such juice pasteurized the same length of time at 180° F."

*Bacillus subtilis* spores survived 190° F. for 30 minutes, but the organism did not develop in either carbonated or still juices.

The death temperatures of yeasts, mold spores and spores of *bacillus subtilis* were not lowered by carbonating at increased pres-

tures. Pressures from 0 to 60 pounds per square inch were used. Juices carbonated to 50 pounds pressure did not permit mold growth, although mold developed in several bottles carbonated at 30 pounds pressure.

## Appendix D.

### REQUIREMENTS OF PECTIN FOR THE COMMERCIAL JELLY-MAKER <sup>1</sup>

By ELOISE JAMESON

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[Reprinted from *Industrial and Engineering Chemistry*, December, 1925]

*A description of an ideal jelly is followed by a discussion of the necessity for using exact proportions of ingredients to make such a jelly. The advantages of the use of pectin in jelly making are then pointed out, with a discussion of methods of adding pectin to make the best jelly with the least amount of pectin.*

*The following characteristics of the pectin preparation suitable for the jelly-maker are then discussed: (1) high jellifying power, (2) standardized jellifying power, (3) a pH value when in solution below 7 but high enough so that it will not make a jelly without additional acid, (4) ability to cause quick setting of jelly, (5) neutrality of color and flavor for manufacturing fine-flavored jellies and jams—for low-grade jellies pectin preparations with fruit flavors may be desired, (6) ability to make a clear solution, (7) ease of use, (8) stability during storage and use.*

A perfect jelly has been often described, but that considered best by the housewife differs materially from that which is most pleasing to the jelly-maker. To satisfy the ideals of the commercial jelly-maker a jelly must have the following qualities:

**FIRMNESS**—The jelly must be firm enough to hold the shape of the glass for some time after being turned out and also strong enough to withstand shipping.

**TEXTURE**—The elasticity must be sufficient so that the jelly if slightly pressed out of shape will return. It must, however, on being cut vertically break on bending over and give a clean broken edge. It must be tender enough to spread well.

**CLEARNESS**—The more brilliantly clear the jelly the more desirable it is.

**SYNERISIS**—Synerisis or separation of liquid from the surface detracts from the quality of the jelly.

**FRUIT COLOR AND FLAVOR**—The jelly should possess the true fruit color and flavor.

### Older Methods of Jelly Making

With the older methods it was often impossible to make a perfect jelly. Not being able to control the pectin content except by the

<sup>1</sup> Presented as a part of the Symposium on Pectin before the joint session of the Divisions of Agricultural and Food Chemistry with the Division of Sugar Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

addition of juice high in pectin, the best way to make a jelly was first to concentrate the fruit juice somewhat and then, after adding the sugar, to boil until the mixture gave an indication of jellying, as tested by one or more of the well known jelly tests—for instance, sheeting from the spoon.

In the finished product, then, the proportions of pectin and sugar varied greatly. Observations in this laboratory, as well as the work of Tarr<sup>2</sup> and others, have proved that these proportions are very important, affecting not only the texture of the jelly but also its success or failure. The long time of cooking darkened the color and often partially destroyed the delicious fruit flavor. With modern methods most of these difficulties can be overcome.

### Proportions of Jelly Ingredients

There is a wide range in the proportions of sugar, pectin, acid and water which if combined will result in a jelly. The jelly will form if the ingredients are dissolved and the solutions mixed cold,<sup>3</sup> but ordinarily they are combined and at least brought to a boil. There is, however, a very narrow range of proportions which can be used to the best advantage commercially.

First, the proposed jelly standards call for a jelly with about 65 percent total solids, most of which are necessarily sugars, cane and invert. This jelly has been found to keep well as ordinarily handled. There is at present a tendency to lower the sugar proportion, and to put into sterile containers and seal hot to increase the yield of jelly. The sugar can be decreased to about 50 percent and still a good jelly will result. However, about a 65 percent sugar jelly will be considered as the standard. With this sugar content the acidity can be varied somewhat. Tarr's work on the pH of jellies has thrown a great deal of light on this. The commercial jelly mixtures on which the pH has been determined in this laboratory have given values within the limits which he determined on good jellies—i.e., 3.0 to 3.54. With too high H-ion concentration there is syneresis, with too low, jelly failure.

The pectin quantities cannot be varied over a very large range without making the jelly either too firm or too weak. The amount of pectin cannot be stated quite so definitely as the acid and sugar, because it depends upon the quality of the pectin in the preparation used. On comparing the quantities of sugar which can be

<sup>2</sup> Del. Agr. Expt. Sta., *Bull.* 134, Tech. No. 2.

<sup>3</sup> Sucharipa, *J. Assoc. Official Agri. Chem.*, 7, 57 (1923).

jellied by each pound of different pectin preparations under the same conditions and with the same proportions of acid and water to each unit of sugar, a tremendous variation is found. This is what makes some of the literature misleading. A pound of a given pectin preparation may jelly only 50 pounds of sugar, while another will jelly 250 pounds of sugar. When by pectin we mean a chemical compound or a substance with a definite jellying power it will be possible to set very positive limits.

### Use of Pectin

As has been pointed out above, definite proportions of jelly ingredients are required. Obviously, since the strength of pectin preparations varies, they must be carefully standardized before they can be used in jelly making. With this precaution taken, it is possible to control carefully the quantities of ingredients and by reducing the time of heating to a minimum to produce almost perfect jams and jellies.

It has been the custom to add commercial pectin solutions after boiling the sugar and juice for a short time to a definite temperature. The mixture has then been poured into final containers in which the acid has already been placed. The dry pectin preparations have usually been mixed with a small amount of sugar and put into solution in the juice. Then the remaining sugar has been added and the whole boiled a short time to a definite temperature, usually 130° C. In some cases the dry preparations have been put into solution and used like the liquid pectin preparations.

These methods are a tremendous gain over the old ones, but still leave room for improvement. For instance, the vacuum method suggested by Noyes might be useful. Heat of any kind hurts pectin and consequently the quality and yield of jelly. If the jelly methods could be improved so that the dissolved pectin, properly sterilized and cooled to a pasteurizing temperature, could be added to the remainder of the jelly ingredients, which has been heated sufficiently to sterilize, and then cooled to the same pasteurizing temperature, more and better jelly would result from the same amount of pectin. At present, commercial jellies are often poured into 30-pound containers very hot. The heat is held until some harm has been done. In fact, jelly-makers use a larger proportion of pectin for jelly packed in large tubs or tins. The injury may be noticed when using a colorless pectin. The jelly around the edge, where the cooling is quickest,

will be clear, colorless and very firm. Toward the center, where the heat is held a long time, the jelly will be softer, showing harm done to the pectin, and yellowed and with a taste indicating some caramelization of the sugar. The acid added in the containers hastens the injurious effect of the heat.

Another suggested improvement would be boiling to a definite calculated weight instead of to a predetermined temperature. This would prevent the differences in final sugar content which occur when a definite temperature is used, owing to the inversion of sugar during boiling. These differences are quite great. There is considerable inversion of sugar when juices containing tartaric acid are used and a larger yield of a less firm jelly is obtained than when less highly ionized acid fruit juices are employed. This results from the raising of the boiling point due to the two molecules of invert sugar in place of the one of cane sugar.<sup>5</sup>

### A Satisfactory Commercial Pectin

Pectin, either pure or mixed with inert ingredients or sugar and acid, has been on the market for a great many years in apple pomace extracts, concentrates, and dry products.

Considerable work has been done on the composition of pectin,<sup>6,7</sup> and this is very valuable to the pectin manufacturer. It has been proved to be an unstable substance, which must be handled with great care to prevent hydrolysis and consequent diminution of its jellying powers. As hydrolysis proceeds and methyl groups are lost, more pectin is constantly necessary to make a jelly of given strength. The quality of the jelly also deteriorates; it loses some of its elasticity and sharp edge. In general, then, a pectin with a high jellying power is more desirable for the manufacturer of jellies.

The manufacturer also requires a constant well standardized pectin. He must be able to use the same amount of pectin, always, and get exactly the same results. The product must then be manufactured from material which will give a uniform product and in a manner which will preserve the quality, or else be mixed with some inert substance to establish a uniform pectin preparation.

The pH of a solution of pectin used in jelly making must be kept above a certain value—about 3.7 in the case of the pectins with which the author has worked, although it may be less with others. Otherwise, a jelly may form before the mixture can be poured into

<sup>5</sup> H. T. Leo, personal communication.

<sup>6</sup> Fellenberg, *Biochem. Z.*, 85, 118 (1918).

<sup>7</sup> Ehrlich, *Chem. Ztg.*, 41, 197 (1917).



the final containers. In fact, the pH should be so high that the jelly mixture can be cooled and remain fluid until the acid is added to make it jelly. The other limit is 7.0, or alkalinity.

An interesting problem presented itself in preparing a pectin satisfactory for jelly manufacturers. Some pectins were found which, although making very firm jellies when set, still jellied so slowly that they were not satisfactory. In jam manufacture it is often desirable to keep whole small fruits suspended in the surrounding jelly. Unless the jelly sets almost instantly when the acid is added the fruit will not be held in place. Also, when large containers of jelly are poured, unless the jelly sets very quickly the high temperature at which the jelly mixture is held so long weakens the pectin. After the pectin has precipitated as a jelly the effect of the heat is very much less.

So it became highly desirable to produce a rapid-setting pectin for the trade. Many factors affect the rate of setting of jelly. Up to a certain point as the acidity increases the rate of setting increases. With a constant amount of the same acid added the following observations were made: As the sugar content increases the rapidity of jelling increases.<sup>8</sup> It may be a function of the solubility of the pectin, because pectin becomes less soluble in sugar syrups of increasing strength. A pectin having a high jelling power also makes a jelly which sets more quickly than that with a less jelling power, even when the two jellies have the same firmness. However, the slight differences produced by these causes do not seem sufficient to explain the great differences between some pectins. It seems possible that there may be some chemical explanation, such, for instance, as the splitting off of a sugar group which might make the difference in solubility and hence in the time in which a jelly sets. A study of the factors which influence the rate of setting of jellies would be well worth while. It is probably better stated as the temperature at which a jelly sets as the jelly is gradually cooling from 103° C. to room temperature after it is poured. In a jelly glass the time of setting may be 15 seconds in one case, in another 1 hour.

Sugar jellies alone have been considered. With glucose jellies the rate of setting is equally important, but for different reasons. The glucose jellies are poured at 82° C., at which temperature there is little injury to the pectin even when the heat is held a long time, but the glucose jelly is handled in large tubs and it is very much more easily packed for shipping after it has set, so an immediate jelly is desired.

<sup>8</sup> Ohm, M. A. Thesis, University of California, September, 1924.

The more tasteless a pectin is, the less it will affect the delicate fruit flavors. For the high-grade jellies a pure pectin is more desirable. With lower grades of jellies oftentimes a fruit flavor carried with the pectin gives an added substance to the jelly, which is an advantage. The same applies to the color of pectin. In high-grade jellies it is undesirable, but often is an aid in cheap jellies.

The clearness of a solution made with pectin is an important characteristic. Most jelly-makers like a brilliant jelly which may be clouded by a pectin making a turbid solution. One manufacturer of very fine jellies and jams, however, prefers that they be not too clear so they will be more like home-made products.

A pectin product must be easy for the manufacturer to use. If a dry product, it must go into solution readily. This quality is influenced by impurities, acids, fineness of grinding, and possibly other factors.

It must not only be easy to handle, but it must be a product with which it is hard to make mistakes. In this respect a liquid product is preferred by some. The jelly ingredients are always weighed. With a liquid pectin preparation a slight mistake in weighing will not affect the jelly so seriously as with the dry preparation, because of a lower concentration of pectin.

Lastly, the product is better if unchanged by atmospheric conditions. Whether liquid or dry it must have the correct acid reaction. It is unstable if alkaline or too acid. The dry pectin preparation has the added advantage over the liquid because a package when opened will not deteriorate even when not all used at one time.

## Appendix E.

### SUGAR LARGELY DETERMINES TEXTURE, FLAVOR AND YIELD OF JELLY

A bulletin (No. 136; Technical No. 3; March, 1924; 29 pp.) on "Fruit Jellies, II. The Role of Sugar," by Lester W. Tarr and George L. Baker, has been issued by the University of Delaware Agricultural Experiment Station, Newark, Del. Its contents are very effectively summarized in the bulletin, as follows:

(1) The texture, flavor and yield of jelly are largely determined by the quantity of sugar that is added.

(2) There is no specific amount of sugar that must be added to insure the successful formation of a jelly.

(3) Other conditions being equal, a weak jelly results from the addition of too much sugar. A tough jelly results from the addition of too little sugar.

(4) The quantity of sugar that may be added varies with the hydrogen ion concentration of the fruit juice. With a constant quantity of pectin (2 g.), it was possible to add 125-130 g. of cane sugar when the hydrogen ion concentration was pH 3.37, 145 g. when hydrogen ion concentration was pH 3.23, and 180 g. when the hydrogen ion concentration was pH 3.10.

(5) As the yield of jelly depends largely upon the quantity of sugar added, it is evident that the yield will vary with the hydrogen ion concentration.

(6) Although the quantity of sugar added may be varied over a wide range, the percentage of sugar that exists in the finished jelly is reasonably constant.

(7) The percentage of sugar present in the finished jellies obtained in these investigations was approximately constant at 69 percent, but increased slightly as the hydrogen ion concentration was increased.

(8) The least concentration of sugar that enabled a jelly to form with the pectin stock solutions employed in these investigations was 64.1 percent, regardless of the hydrogen ion concentration of the solution. However, increasing the hydrogen ion concentration did result in increased jelling properties.

(9) The concentration of sugar that exists when a jelly is formed is shown to be approximately that of a saturated solution of sugar. The slight increase in sugar concentration that occurs as the hydrogen ion concentration increases *is due to the greater solubility of sugar in the increased quantities of invert sugar that are formed.*

(10) The quantity of invert sugar formed during the ordinary jelly making process is a function of the hydrogen ion concentration and of the time of heating. If the time is constant, the quantity of invert sugar formed increases as the hydrogen ion concentration increases. If the hydrogen ion concentration is constant, the quantity of invert sugar formed increases as the time of heating increases.\*

(11) The inversion progresses at a fairly uniform rate for a given hydrogen ion concentration.

(12) Approximately the same quantity of invert sugar is formed for a given hydrogen ion concentration, regardless of the concentration of sugar employed.

(13) The hydrogen ion concentration is suggested as a means for controlling jelly formation and uniformity of product.

(14) A new pectin product is described which may have commercial possibilities.

(15) Jelly formation is conceived of as occurring in the presence of a saturated, or an approximately saturated, solution of sugar. The function of the sugar may be that of a dehydrating agent. The acid is believed to control the precipitation of the pectin in the jelly form.

\* Authors think it advisable to add the sugar during last half of boiling down process to prevent too much inversion (and loss of sucrose).

## Appendix F.

### ELABORATE RESEARCH ON THE MANUFACTURE OF MAYONNAISE

By PROF. MARK of SIMMONS COLLEGE

*[There was published in THE SPICE MILL for August, 1922, a note on experiments on emulsification in mayonnaise by Professor Kenneth L. Mark, of Simmons College, Boston, Mass., which aroused considerable interest in the trade and requests were made for a fuller statement covering these experiments, with particulars of the developments as anticipated in the note. Through the courtesy of Professor Mark, THE SPICE MILL was enabled to satisfy these requests by publishing, in the March, 1923, issue, a full statement of the initial experiments and supplemental report on the research. Since that presentation the demand for the article has been so great that the particular issue of THE SPICE MILL has become exhausted, and in order to give those interested an opportunity to utilize the information contained therein we are reprinting here the article in full.]*

#### Emulsification in Mayonnaise

The following is only a preliminary report of work which is being done on this subject. Enough progress has not yet been made to formulate a rule of procedure which will insure unvarying success in making the dressing.

The actual work has been to follow the process of emulsion by taking samples every few seconds during the beating together of the ingredients and observing these samples under the microscope. In general the results have been those which would be predicted from our knowledge of the principles of emulsion. Before taking up a report of these results a brief outline of what may be expected will be presented.

Mayonnaise is a stable emulsion of oil in the water derived from the yolk of egg and from vinegar. The conditions necessary to make an emulsion which will remain permanent are well known. In addition to the two immiscible liquids, one of which is broken up or dispersed in the other by beating and shaking, there must be present also a third substance, the emulsifying agent, which is usually a colloid or a very fine suspension. In mayonnaise the emulsifying agent is the protein in the yolk of egg.

The conditions which must exist in order that an emulsion remain stable have been extensively studied by Bancroft and others.

This, however, is not the problem which confronts the maker of mayonnaise, for when the dressing is once made it usually keeps. Failures occur in making the mayonnaise. The conditions necessary to produce an emulsion, which when finished remains stable, have not been thoroughly investigated.

The factors involved are obviously:

(1) The physical properties of the substances used, of which surface tension and viscosity are the most important. These properties may in turn be modified by such factors as temperature and mutual solubility.

(2) The proportions of the ingredients.

(3) The manner of beating or shaking.

Preliminary experiments showed, as would be expected, that variations produced by using different kinds of oil, or by working at different temperatures, were slight compared with the factors of proportion and manner of beating.

If we picture for a moment what happens when we beat together two immiscible liquids, it is plain that the beating breaks up both of them, but the particles of one will unite as fast as they are broken up, and this liquid will remain continuous and become the disperse medium of an emulsion; whereas the particles of the other liquid are being broken up faster than they unite and hence becoming smaller and smaller constitute the disperse phase of the emulsion. When the beating ceases these particles may again unite, no permanent emulsion being formed, or if the proper emulsifying agent is present they may remain dispersed, thereby producing a stable emulsion.

If we beat a mixture containing a very small quantity of liquid A in a large quantity of liquid B, it is obvious that the particles of A will become widely separated, and thus will unite more slowly than the particles of B. We shall have an emulsion of A in B.

If we consider a series of mixtures in which there is a constantly increasing proportion of A, we shall pass through some rather indeterminate mixtures to the cases where B is dispersed in A. It is in these transition mixtures that other factors than proportion, such for example as viscosity and manner of beating, may have a determining influence on the kind of emulsion formed.

Thus intermittent beating has been shown in some cases to produce emulsification much more rapidly than continuous beating, since time is given during the period of rest for the particles of the emulsion medium to reunite.

In making mayonnaise we must produce an emulsion of oil in

water, since egg-yolk stabilizes this emulsion but does not stabilize an emulsion of water in oil. Attention was first directed, therefore, to determining the maximum amount of oil which could be emulsified in a given amount of egg-yolk in successive additions and under definite conditions.

Into 10 cc. portions of yolk were beaten various volumes of oil. The beating was done in a small casserole with a very small egg-beater for 100 seconds, with a pause of 10 seconds at the end of each 10 seconds. During each period of rest, a sample was taken out which was later viewed under the microscope.

The egg-yolk itself is an emulsion to begin with. At a magnification of 660 diameters, each globule of oil appears about 0.2 mm. in diameter. When 1 cc. of oil was beaten with 10 cc. of egg, the first sample, that taken after 10 seconds, showed the oil to be dispersed in the egg in drops of various sizes. In the sample taken after 20 seconds the drops of oil were more uniform, and in the sample taken after 30 seconds they were quite uniform, and only slightly larger than the oil globules in the original eggs. Further beating produced no change.

When, however, 6 cc. of oil were beaten with 10 cc. of egg, the first sample showed masses of yolk floating in a sea of oil. Further beating served only to diminish the size of the yolk particles and never produced a stable emulsion.

A large number of trials were now made varying both the proportions of the ingredients and the total amounts, with the result that for 10 volumes of egg, 3 or less volumes of oil were always emulsified, while 4 or more volumes never were.

To determine how much oil could be used in the second addition, 3 volumes of oil were emulsified in 10 volumes of egg and varying amounts of oil were then beaten into samples of this emulsion. Again 3 volumes of oil was the maximum amount that could always be taken up by 10 volumes of the emulsion. The corresponding amounts for the third and fourth additions were 4 volumes and 4.5 volumes respectively. Further additions of oil were not attempted as the dressing had become too stiff to beat conveniently.

The successive volumes of oil which could be added to 10 volumes of egg were thus 3, 4, 7 and 12 volumes.

A dressing was made with those proportions, keeping all the ingredients at 55 C., and the experiment was also carried out in ice water. In both cases stable emulsions were formed.

Constant beating gave the same results as intermittent beating when these proportions were used.

Next the effect of adding vinegar to the egg before beating was studied. The addition of vinegar, which reduces the viscosity very considerably, increases the proportion of oil which can be added at the first installment, but the amounts which can be used in subsequent additions rapidly approach the values of egg alone, as the mixture becomes stiffer.

In summarizing the work, so far, it appears that if the proportion of unemulsified oil to that of the emulsion which exists at the moment is kept below a certain maximum, a stable emulsion is always formed. In other words, in making mayonnaise, if the oil is added slowly enough a successful dressing is produced no matter what the other conditions may be.

The work is being continued.



## Appendix G.

### REPORT ON A COOPERATIVE RESEARCH ON MAYONNAISE<sup>1</sup>

In accordance with the request of the Research Section of the American Home Economics Association made in July, 1921, a co-operative research on mayonnaise has been carried on during the past year. Those who have submitted reports are Professors S. DeBorah Haines, of the University of Chicago; Agnes Johnson, of the University of California; Esther McGinnis, of the University of Maine; Alice M. Child, of the University of Minnesota; Anne E. Smith, of the University of Indiana; Jessie Whitacre, of the Agricultural College of Utah; Leila W. Hunt, of the State College of Washington, and Kenneth L. Mark, of Simmons College, Boston. The following report is arranged under the various problems which have been studied, rather than as summaries of the work of each investigator separately:

**1. Temperature.** Professor McGinnis tried variations in the temperature at which standard dressings (proportions not given) were prepared and found that the stability of the dressing was unaffected up to 38° C.

Professor Mark, working on the maximum amount of oil which could be emulsified upon successive additions of oil, obtained the same results at 0° C., at 50° C., and at intermediate temperatures.

It seems evident that the effect of temperature is negligible within the temperatures ordinarily existing during the preparation of mayonnaise.

**2. Kinds of Oil.** Professor McGinnis succeeded in emulsifying in 15.6 grams of egg-yolk varying amounts of different kinds of oils as follows: Pure olive oil—Italian 296 grams, California 344 grams, Spanish 441 grams, French 450 grams; "Mazola" oil 399 grams; and "Wesson" oil 432 grams.

Professor Child, however, reports the reverse order in the last named oils, with "Douglas" oil intermediate between them, and Professor Mark found no difference between "Wesson" oil and "Mazola" oil.

<sup>1</sup> Originally published in *The Spice Mill*, August, 1924.

Professor Johnson, also, reports no difference in the quality of the final product, whether "Wesson" or "Mazola" oil was used.

In none of the experiments were the chemical composition or the physical properties of the oils studied, so that the cause of such variations as were found is in doubt. Further study is desirable to ascertain why only about two-thirds as much Italian and California olive oils can be emulsified as other kinds of oil.

**3. Age of Eggs.** Professor Johnson made emulsions with eggs of different ages. Proportions and conditions which produced a satisfactory and stable dressing with eggs one day old gave equally good results with eggs 18 days old, but eggs 42 days old made a poor emulsion which completely separated in 4 days. "Store" eggs of unknown age gave equally poor results.

Professor Mark tried the use of cold storage eggs, the yolks of which appeared watery, and was able to emulsify only about one-third as much oil as with fresh eggs.

Some large scale manufacturers use "broken out" frozen eggs and a study of the efficiency of these eggs as compared with fresh eggs would be valuable.

**4. Substitutes for Egg-Yolk.** Professor Child used egg-white instead of egg-yolk and found its efficiency as an emulsifying agent to be about one-quarter that of the yolk, and the efficiency of the whole egg to be that of the sum of the yolk and the white separately.

Professor Haines added flour in the form of thick white sauce (compound of 1 quart of milk to 4 ounces of flour) to egg in the proportion of 8 yolks to one pint of white sauce. She obtained a palatable dressing which contained twice the amount of oil which the egg alone would stabilize. This dressing, however, moulds very quickly and thus the advantage of the addition of flour is questionable.

Professor Haines tried, also, the addition of gelatin and reports its use as unsatisfactory, since the emulsion broke and the oil separated out upon standing. She used, however, comparatively large amounts of gelatin, enough so that the mixture stiffened upon cooling. The gelatin probably extracted water from the emulsion film, which was thus destroyed and caused the oil to separate. Professor Mark obtained very satisfactory results with gelatin but he used only 3 grams to a liter of the finished product. The gelatin was added by dissolving it in the vinegar. Dressing with the gelatin in it withstood transportation and long standing better than without it.

**5. Initial Addition of Oil.** Professor Smith found that the maximum volume of oil which could be added at one time and become emulsified in 10 cc. of egg-yolk was 5.5 cc. when the beating was continuous. If, however, the mixture was beaten for periods of 10 seconds with periods of rest of 15 seconds, 6 cc. could be used; and when the period of rest was increased to 25 seconds, 6.5 cc. could be emulsified. Microscopic examination showed that permanent emulsions were formed only when the oil had been broken up into globules of approximately uniform size and distribution.

Professor Whitacre and Professor Mark carried on experiments with periods of 10 seconds each of beating and of rest and they both found the critical volume of oil to be between 3 cc. and 4 cc. for 10 cc. of egg-yolk.

**6. Intermittent Beating.** Professor Smith, as stated above, was able to increase the amount of oil emulsified by allowing short periods of rest during the beating, and Professor Mark obtained similar results. Indeed this effect of intermittent beating is well recognized in the preparation of many emulsions. Moreover, it is common knowledge that when mayonnaise has been standing for some time more oil may be readily embodied in it by only a few revolutions of the beater. All of these facts point to the great importance of intermittent beating in making mayonnaise. Much more work on the effect produced by periods of rest of considerable length should be done and will be valuable, both from a practical standpoint and as bearing on the cause of the efficiency of intermittent beating in making emulsions.

**7. Speed of Emulsification.** Professor Whitacre proved, as would naturally be expected, that small amounts of oil were emulsified sooner than large amounts, but she showed that the time is not directly proportional to the amount of oil. One cubic centimeter of oil was emulsified in 10 cc. of egg in less than 10 seconds, 2 cc. in 20 seconds, 2.5 cc. in 40 seconds, 3 cc. in 80 seconds, and 3.5 cc. were not emulsified at the end of 180 seconds. Although these data are too few in number to serve as a safe basis for making a generalization, they point to the relation that the time, or rather the total number of revolutions of the beater, is proportional to the cube of the volume of the oil added. This is a relationship which might be predicted, because if a number of particles were to be distributed evenly along a line, the time required would be proportional to the number of particles; but if they were distributed evenly on a surface, the time would be proportional to the square of the number

of particles; and if distributed in a volume, to the cube of the number. Experiments will be of interest to determine the truth or the falsity of the proposition that the time required for emulsification varies with the cube of the volume emulsified.

This relationship may explain some of the frequent failures in making mayonnaise. For example, using Professor Whitacre's figures, in 80 seconds only 3 cc. of oil could be emulsified if added all at once; but in 80 seconds 8 cc. could be emulsified if added in 2 cc. portions, and a still larger amount if added in still smaller portions. On the other hand, if a portion of 3.5 had been added, no emulsion at all would have been produced. It follows, therefore, that the oil should be added in a small steady stream during the beating rather than in separate portions to be successively beaten in.

**8. Maximum Proportion of Oil to Egg.** Professor McGinnis, as already stated, found the final maximum proportion of oil to egg to differ with different oils; but taking the value for "Wesson" oil, 28 cc. of oil could be emulsified in one cc. of egg-yolk.

Professor Child worked with a complete dressing. She found that when one volume of egg was diluted with 8 volumes of vinegar, 40 volumes of oil could be taken up. This is in fairly good agreement with the results of Miss French, working at the New England Kitchen in Boston, who reports a maximum of 48 volumes of oil to one of egg diluted in the same ratio as Professor Child's. This agreement is of interest, moreover, since Professor Child was working on a very small scale and Miss French was using over one hundred times the quantities in a power beater.

Professor Johnson made a complete dressing in which 90 volumes of oil were used to one of egg, but 15 volumes of vinegar were employed. This proportion is not discordant with the preceding results, since the volume of the emulsifying agent, namely the diluted egg, was nearly doubled.

No one has reported any attempt to determine how far this dilution of egg with vinegar or water may be carried and still serve as a satisfactory emulsifying agent. This problem appears to be one of some interest and importance.

**Summary.** It will be observed that considerable and valuable data have been collected, but that small progress has been made toward a knowledge of the underlying physical principles involved in making mayonnaise. It has been shown (1) that within ordinary limits temperature has little effect; (2) that the kind of oil, the age

of the egg, and the addition of substitutes for egg-yolk are of consequence; but (3) that these factors are not so important as the rate of addition of oil and the manner of beating. A number of directions in which the investigation may be continued are pointed out.

## Appendix H.

### LABELING BEVERAGES AND BEVERAGE MATERIALS UNDER THE FEDERAL FOOD AND DRUGS ACT \*

Several court decisions have been handed down recently which are of such importance in their possible application to the beverage industry that all bottlers, officers of beverage supply houses and others connected with the industry should be fully informed regarding them. Moreover, the Bureau of Chemistry is constantly commenting, from the standpoint of the Federal Food and Drugs Act, on the suitability of the labeling of specific beverages and beverage materials, and it is highly desirable that the trade and State food and drug officials be advised in a general way as to the progress which is being made in the enforcement of the act, as applied to these products.

One of the court decisions referred to above is that handed down recently by the Supreme Court of the United States of America, *Petitioner vs. Ninety-five barrels (more or less) alleged apple cider vinegar*. Mr. Justice Butler in delivering the opinion of the court made the following statement, among others:

"The statute is plain and direct. Its comprehensive terms condemn every statement, design, and device which may mislead or deceive. Deception may result from the use of statements not technically false or which may be literally true. The aim of the statute is to prevent that resulting from indirection and ambiguity as well as from statements which are false. It is not difficult to choose statements, designs, and devices which will not deceive. Those which are ambiguous and liable to mislead should be read favorably to the accomplishment of the purpose of the act. The statute applies to food and the ingredients and substances contained therein. It was enacted to enable purchasers to buy food for what it really is."

Even the layman will immediately recognize that the above statement, coming from the Supreme Court of the United States, is of the greatest importance, since it will assist materially in determining whether or not the act is being violated when vague and ambiguous statements which are liable to mislead are made on the labels of beverages, beverage materials and other food.

\* Based on a paper presented at a recent meeting of food officials at Philadelphia, Pa., by J. W. Sale, Chemist in Charge, Water & Beverage Laboratory, Bureau of Chemistry, U. S.

The lower courts have taken cognizance of the above quoted statement emanating from the Supreme Court as indicated by the court's ruling in the case *United States of America vs. McIlvaine Brothers*, a corporation. In this ruling Judge Dickinson made the following statements, among others:

"Fortunately, the Supreme Court of the United States in the *Apple Cider Vinegar* case (No. 599, October Term, 1923), not yet reported, has charted the course to be followed. The general rule is that the Act of Congress should be so read as to further the accomplishment of its purposes, and that not only any branding which is misleading or liable to mislead but also any which is ambiguous should be visited with the condemnation of the Act. Following the course thus indicated, we encounter the fact finding now made that the branding first given this product has the vice of ambiguity in that although it is not expressly stated that the product is what is known to the trade as powdered colocynth and it is stated that it is powdered colocynth apple, yet it is none the less true that the difference in the product is not so stated as to command attention to the fact that there is a difference but is so stated that the difference may be overlooked and the purchaser be buying one product with the thought in his mind that he is buying another. As we interpret the spirit and true meaning of the ruling cited, it is that a branding which is misleading because of its ambiguity is as much within the inhibition of the statute as if it was misleading in statement."

During the last five years, so many claims of one sort or another have been made which are designed to lead consumers to believe that most beverages contain a high content of fruit, or fruit juice, that one is rather skeptical nowadays with regard to the truthfulness of placards advertising real fruit beverages. It is indeed an unfortunate situation when people are unable to distinguish from the crown caps, bottle labels, soda fountain hangers, bill boards or newspaper advertising, between beverages which contain substantial amounts of fruit, those which are merely fruit flavored, and those which are artificially flavored. It can not be denied that there is a marked tendency among supply houses and among bottlers and proprietors of soda fountains to advertise their products in such a way as to make them appear better than they really are; that is, imitation fruit beverages are represented to be genuine; beverages which are merely fruit flavored are represented to be beverages which contain substantial amounts of fruit juice; and beverages which contain substantial amounts of fruit juice are frequently represented to be 100 percent fruit juice.

The Federal Food and Drugs Act and most State laws are sufficiently broad to prevent a considerable part of such misinterpretation, and it is up to the enforcement officials to apply the laws in such a way as to give the purchaser a square deal. The interstate shipment is the first of a series of negotiations, and if the labeling of the interstate shipment is truthful, then the bottler or the soda fountain pro-

prietor will have no excuse to misbrand the beverages which he manufactures from the flavoring syrup shipped in interstate commerce, and State and city inspectors will have a source of information as to the composition of the finished products. It has been represented to the Bureau of Chemistry on several occasions that if an imitation fruit flavor is labeled by a distinctive name such as "Lot No. 4," no one is deceived or misled because the purchaser knows what he is getting and the goods do not reach the ultimate consumer. However, if imitation flavoring preparations are not required to be labeled as imitations in strict compliance with the law, then the opportunity is lost of informing State inspectors of the character of the flavor, and of preventing the bottler from excusing the misbranding of his beverages on the ground that he thought he was using true fruit flavor.

### Classification of Beverages

In considering the legality of beverage labels, we have found it useful to divide beverage flavors and beverages into approximately four main classes, as follows:

Class 1—Fruit juice.

Class 2—Soda fountain syrups and beverages made from them.

Class 3—Bottlers' flavors and bottlers' carbonated beverages.

Class 4—Powdered flavors for general household use.

#### *Class 1—Fruit Juice Beverages*

In Class 1 we have (a) straight fruit juices such as apple juice or cider and grape juice, etc., and (b) fruit juice with added sugar or added acid, including loganberry juice, some grape juices and the like.

Most of the beverages in Class 1 are being labeled in compliance with the law, and when they are not, the regulatory official will have little difficulty in deciding what constitutes suitable labeling for them.

Several years ago complaints were made to the Bureau that grape juice was being adulterated with artificial flavor. The Bureau made a careful examination of the majority of bottled grape juices on the market and did not find any that contained synthetic flavor. Generally speaking, the presence of added sugar should be declared on the label of grape juice and other fruit juices, in strict accord with Item 187, which reads as follows:

"Sugar added to grape juice, loganberry juice or other fruit juice should be declared upon the label. Articles labeled as grape juice,



loganberry juice, or as the juice of any fruit, are adulterated if they contain added water." Added acid should also be declared on the labels of bottled fruit juices. The labels of these products may properly bear designs of fruit such as clusters of dripping grapes.

*Class 2—Soda Fountain Syrups and Beverages Made from Them.*

In Class 2, we have (a) concentrated fruit juice; (b) fruit syrups; and (c) fruit flavored syrups.

(a) *Concentrated Fruit Juice.*—The first subdivision, (a) concentrated fruit juice, is represented by commercial concentrated orange juice filtered and unfiltered. This juice is prepared by evaporating either filtered or unfiltered orange juice in glass-lined vacuum pans under a vacuum of at least 28 inches to a density of 72° Brix measured at a temperature of 38 to 40° C. The article contains no added sugar or other added ingredients, and the directions for use are as follows: Add to one volume of the concentrated juice three-quarters gallon simple syrup, 9¼ gallons ice water, and from 0.005 to 0.01 percent of emulsified oil of orange. The resulting beverage will contain concentrated orange juice equivalent to 65 percent of raw juice. It is, of course, proper to make claims of content of fruit juice in articles of this type and to employ designs of fruit on the label. It is believed that you will have no difficulty in deciding as to what constitutes a proper label for articles of this kind, since there is not involved the question as to whether or not they are imitations.

(b) *Fruit Syrups.*—We now come to subdivision (b) fruit syrups, in Class 2, about which there may be some measure of doubt as to suitable labeling. Pending the formulation of definitions and standards for fruit syrups, the Bureau holds that an article designated without modification as a fruit syrup should contain not less than 33⅓ percent by weight of fruit juice and not less than 50 percent by weight of sugar, with no added water or other ingredients. This definition was formulated several years ago and up to the present time has successfully withstood the bombardment of many objections by firms who wished to employ something less than the 33⅓ percent by weight of fruit juice in their products, although the definition has never been tested in court.

One of the most important questions that have been raised in connection with this definition has been that of the dilution to which the fruit syrup is to be subjected. Some fruit syrups intended for use at soda fountains are subjected to a dilution of only 1 to 5 or 6 in the

manufacture of the finished drink, while others are subjected to a dilution with simple sugar syrup of 1 to 2 or 3 and again to a dilution of 1 to 5 or 6 water, making a total dilution of approximately 1 to 10 or 18. Still other fruit syrups are subjected to even higher dilutions. Does the 33 $\frac{1}{3}$  percent standard apply equally to all syrups regardless of their dilution? Our reply to such inquiries is that a decision as to the propriety of the labeling must be based on the complete composition of the product, and upon the character of directions which appear on the label or which are supplied separately to bottlers. If the beverage made from the fruit syrup is to be labeled in such a manner as to indicate that it contains fruit juice, then the fruit syrup should contain not only the required 33 $\frac{1}{3}$  percent of fruit juice, but should be employed in such a manner that the beverage manufactured from it according to the directions of the manufacturer will contain a substantial amount of fruit juice. In other words, a syrup which is so reinforced with essential oils that it is necessary to dilute it 10 times or more before it is fit to drink is considered to be misbranded if labeled as a fruit syrup even though it contains 33 $\frac{1}{3}$  percent of fruit juice. This comment applies also to bottlers' flavors in Class 3.

Item 357, "Labeling of Clear and Cloudy Fruit Flavored Beverages," which applies to genuine and imitation fruit beverages, reads as follows:

"Terms such as 'ade,' 'squash,' 'punch,' 'crush,' and 'smash' can be applied properly only to beverages, either still or carbonated, which contain the juice or edible portion of a fruit. These terms should not be applied to products flavored only with essential oils or essences, unless plainly labeled as imitations. The Food and Drugs Act requires an imitation to be labeled with the word 'imitation,' together with a statement showing wherein it is an imitation, which ordinarily requires a declaration of those ingredients, such, for example, as essential oil, citric acid, and artificial color, giving the article its principal characteristics.

"It is further held that any turbid or 'cloudy' orange, or other fruit-flavored beverage, which does not contain either an appreciable quantity of the juice or the edible portion of orange or other fruit named, should be labeled plainly as an imitation."

Most fruit syrups contain added acid and color and the presence of these added ingredients should, of course, be declared on the label in a plain and conspicuous manner. There are quite a few products of this class on the market and they are high grade preparations. The labels of these products, in common with the labels of straight fruit juice and of concentrated fruit juice, may properly bear designs of fruit. It is quite important, however, that the labels of these products do not mislead the purchaser into believing that he is getting a concentrated fruit juice. The viscosity of fruit syrups and their general

appearance are such that it is comparatively easy to mistake them for concentrated fruit juices. The word "syrup" on products of this type is considered to explain satisfactorily the presence of added sugar.

(c) *Fruit Flavored Syrups*.—This brings us to a consideration of subdivision (c) fruit flavored syrups, in Class 2. To this class belong syrups flavored with essential oils or with fruit juice which is present to a lesser extent than 33½ percent by weight or with flavor derived wholly and without chemical change from fruit. These products should have the characteristic flavor of the fruit after which they are named and they should be plainly designated as fruit flavored syrups. From one point of view, when orange extract or orange emulsion is added to a sugar syrup, there is produced an orange syrup. However, owing to the fact that the name "Orange Syrup" may lead some into believing that the article is orange fruit syrup, we much prefer that articles of this sort be designated plainly, as orange flavored syrups.

It is customary to employ artificial color in fruit flavored syrups for the reason that there is not sufficient of the fruit present in the articles to give them the desired color, and when artificial color is used it should be declared in a plain and conspicuous manner. If it is proposed to add artificial flavor, in addition to artificial color, then in practically all cases there is produced, from the standpoint of the law, not a fruit flavored syrup artificially flavored and colored, but an imitation fruit syrup, which should be labeled with the word "imitation" and the explanatory statement. It is conceivable that so little synthetic flavor may be added to products of this type that the predominating flavor of the article is genuine fruit flavor, but as a matter of fact, owing to the great difference in flavoring power between the natural fruit flavors and synthetic fruit flavors, the amount of synthetics which are ordinarily used is such that the predominant flavor of the resulting product is due to the artificial flavor rather than to the natural flavor.

In such cases, and they constitute a vast majority, the article which we have to consider is an artificially flavored and artificially colored sugar syrup with only a negligible amount of true fruit flavor. A product of this type is unquestionably an imitation under the law and should be labeled as such in strict accord with the law, as interpreted by regulation 20 (a) in Circular 21, which, in order to refresh your minds, I will read to you. Regulation 20 (a): "An imitation shall bear on the label the word 'imitation,' and, in addition, a clear statement of the principal or essential ingredients of the article." The beverages made from fruit flavored syrups are of course, merely fruit flavored

beverages and should be labeled in such a manner that they will not be mistaken for beverages containing substantial amounts of fruit juice. Fruit flavored beverages look and taste so much like fruit juice products that it is easy to palm them off as fruit drinks.

We receive many inquiries as to the propriety of labeling a sugar syrup flavored with cocoa as chocolate syrup. Oftentimes, these syrups contain added vanillin. It has long been the practice to label articles of this type as chocolate syrups, and pending the adoption of standards for such products, the Bureau has advised correspondents that it is not disposed to object to the labeling of soda fountain syrups made from sugar and water and powdered cocoa as chocolate syrup, provided the article contains not less than 50 percent by weight of sugar and has a substantial chocolate flavor.

### *Class 3—Bottlers' Flavors and Bottlers' Carbonated Beverages*

Item 357, to which reference has already been made, applies to products of Class 3 also. While this item refers to beverages specifically, it may be applied in principle to the flavors from which beverages are manufactured. Bottlers' flavors may be divided into the following subdivision, those made (a) from citrus or other essential oils; (b) from extractives such as ginger ale, root beer, etc.; (c) from genuine fruit flavors; (d) from imitation fruit flavors.

(a) *Bottlers' Flavors Made from Citrus or Other Essential Oils.*—Bottled sodas flavored with citrus oils such as orange, lemon and lime sodas, may be designated properly by the name of the fruit, provided they are not cloudy, thus simulating the appearance of fruit juice and provided further that no claims of fruit juice content are made for them in collateral advertising, such as soda fountain hangers, billboards, newspapers, magazines, etc. Specific authority is not granted by the Federal Food and Drugs Act to develop action based on misleading claims made in collateral advertising. However, if statements are made on the labels of interstate shipments, which are capable of more than one interpretation, it is our custom to accept the meaning conveyed by the manufacturer in his collateral advertising. In this way collateral advertising may sometimes prove quite useful. Designs of fruit should not be placed on the labels of products belonging to this subdivision since at most they contain merely a little fruit flavor and do not contain any fruit juice, as such designs would readily lead one to believe.

(b) *Bottlers' Flavors Made from Extractives.*—With regard to sub-

division (b) it is believed that little discussion is necessary for the reason that the Bureau has issued standards for ginger ale and sarsaparilla. The Bureau has advised correspondents that it will take no action against sarsaparilla because it contains undeclared caramel color, pending a reconsideration of the standard for sarsaparilla in Circular 136 by the Joint Committee on Definitions and Standards. There may be some question as to the proper labeling of root beer. No standards have been promulgated for root beer or for birch beer. Pending the formulation of such standards, the Bureau has advised correspondents that it will take no action against root beer or birch beer which contains undeclared caramel color, provided the articles otherwise meet the requirements of the Federal Food and Drugs Act.

(c) *Bottlers' Flavors Made from Genuine Fruit Flavors.*—The number of beverages belonging to subdivision (c), that is, those whose flavor is true fruit, seems to be gradually increasing. This is a field for careful research. We have had occasion to doubt that some of the flavors alleged to be true fruit are derived wholly and without chemical change from fruit, but this is a rather difficult matter to prove. It is a comparatively simple matter to take, for example, some dried peaches and to extract them with dilute alcohol and to fortify the product obtained with minute amounts of synthetics. When such a product is labeled as a true fruit flavor, it is difficult indeed for the chemist to detect the sophistication; in fact, it is impossible to do so if he has at hand only samples of the finished beverages.

Information which we have obtained in connection with the enforcement of the Federal Food and Drugs Act has convinced us that practically all of the so-called grape flavors for bottlers' use are in fact grape wine to which has been added oil of cognac and methyl anthranilate. Sometimes there is used in place of the oil of cognac a distillate of the skins, leaves and twigs of the grape. Such a product, to our mind, is not grape flavor, but is essentially an imitation grape flavor and should be labeled in strict accord with the law as interpreted by regulation 29 (a). Grape wine flavor is not grape flavor and is not considered to be such by the average person, but, on the contrary, is generally recognized as being an entirely separate article from grape flavor. So far as I am aware, there are no true grape flavors for bottlers' use on the market, although there may be several that are alleged to be of this type. An article which is entitled to be labeled "grape flavor" without modification should be derived wholly and without chemical change from grapes or grape juice.

(d) *Bottlers' Flavors Made from Imitation Fruit Flavors.*—A great many bottlers' flavors and bottled sodas belong to subdivision (d) imitation fruit beverages. Bottled sodas which are artificially flavored and colored in imitation of a fruit drink are, without doubt, imitations under the act, and should be labeled with the word "Imitation," which, in our opinion, should directly precede the name of the fruit and should be in type of approximately the same size and prominence as the name of the fruit. Artificial color, when present in beverages in Class 3, should be declared plainly and conspicuously on the label.

*Class 4—Powdered Flavors for Household Use.*

These products in Class 4 generally consist of a fruit acid such as citric or tartaric, sugar, and a coal tar or vegetable dye. The great majority are imitation fruit preparations and should be labeled as such without equivocation. However, an important exception is powdered lemon juice, manufactured by the spray process. It is believed that there will be little difficulty in deciding as to suitable labels for products of this class. Of course, all of these beverages and beverage preparations are food and should bear a suitable declaration of quantity of contents, in accordance with Regulation 26 in Circular 21 and with Item 382.

Other items of interest in connection with the labeling of beverages are the proper use of distinctive names, the use of names such as punch, julep, nectar, etc., the question of caffeine, and of saccharin, etc. A full discussion of all of these points would lengthen this paper unduly. The Bureau is always ready and pleased to answer inquiries regarding the labeling of beverages and other food. The exchange of opinions along this line can not fail to be of mutual advantage.

Author's Note: The "Items" referred to above are opinions and decisions published in various "Service and Regulatory Announcements" issued by the U. S. Bureau of Chemistry in connection with the duties imposed upon said Bureau by the Food and Drugs Act. "Circular 21" is the pamphlet giving the "Rules and Regulations" for the enforcement of the Food and Drugs Act.

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